A STUDY OF THE IDENTIFICATION OF CERTAIN CLAY MINERALS BY X-RAY DIFFRACTION

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MAY 1953

THESIS
C515

A STUDY OF THE IDENTIFICATION OF CERTAIN CLAY MINERALS

BY

X-RAY DIFFRACTION

Submitted to the Faculty of Rensselaer Polytechnic Institute
in
Partial Fulfillment of the requirements for the Degree of
Master of Civil Engineering

by

W. F. Cline
II
and
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May 1953

Thesis
C515

ACKNOWLEDGEMENTS

The authors wish to extend an expression of sincere appreciation and gratitude to their faculty adviser, Professor E. J. Kilcawley, Head of the Division of Soil Mechanics and Sanitary Engineering, Department of Civil Engineering, Rensselaer Polytechnic Institute, for the many occasions wherein he provided advice, consultation and encouragement during the preparation of this thesis. Moreover, with the completion of a program of graduate study in Foundation Engineering and Soil Mechanics under his direction, the authors wish to convey to Professor Kilcawley their personal feeling of admiration and respect for him which he has caused to be developed during the period in which they had the privilege of being his students.

To Doctor Arthur A. Burr of the Department of Metallurgy, the authors wish to express their appreciation for his generous assistance throughout the work particularly in connection with the use of the X-ray and photographic apparatus and facilities.

To Assistant Professor J. E. Munzer and to Instructor William Kelleher of the Division of Soil Mechanics and Sanitary Engineering, the authors are indebted for the valuable assistance and services which they furnished through some of the most difficult portions of the work.

Further acknowledgment is made for the most helpful assistance furnished throughout the work by the following:

Nicholas E. Doyle, Jr., Research Associate in Metallurgical Engineering

John N. Ramsey, Research Associate in Metallurgical Engineering

Last but by no means least, appreciation is expressed to Commander J. A. Bentley, (CEC) USN, for his whole-hearted interest and cooperation in making available certain invaluable reports, data and core samples, in connection with the general land subsidence at the U. S. Naval Shipyard, Long Beach, California

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SECTION I

INTRODUCTION

OBJECTIVE: This thesis has been prepared with the following primary objective:

(a) To develop a quick and accurate means for the identification of clay minerals thru X-ray diffraction patterns obtained from standard samples.

Other objectives are:

(b) To evaluate the methods and techniques developed by Dearth and Williams (3) for the preparation of sample specimens.

(c) To attempt identification of a number of unknown sample materials by means of X-ray diffraction.

(d) To present an extremely complicated subject in such a manner that it can be understood by the average Civil Engineer. While it is recognized that the majority of Research papers are written for the benefit of other investigators in similar work, it is felt that a better understanding of fundamental considerations on the part of the practicing engineer will considerably increase their appreciation of the problem involved.

Modern literature concerning research in the field of Soil Mechanics makes frequent reference to various new methods for the qualitative and quantitative determination of clay minerals. These include differential thermal, flame photometer, spectrographic and X-ray diffraction analyses. These developments are of direct and immediate interest to the Soil Mechanics investigator. Many of them are also of considerable, though indirect benefit to the construction engineer. New analytical methods at once become the tool whereby much needed fundamental research becomes possible in connection with an essential construction medium about which so many know so little.

In this enlightened age of the art of engineering, who will say that we know all the answers to our foundation problems? For example, it has recently been reported that every air field which has been built in Europe since the end of World War II requires urgent major repairs or else faces abandonment as being unfit for use because of a lack of appreciation of the foundation problems involved.

The soil scientist's task is to develop basic concepts and delineate primary soil relationships which the engineer can then apply with some degree of intelligence.

The work and experimentation necessary to develop an understanding of the clay material of the soil is of relatively recent origin, having its beginning as recently as 1930. This work has been very closely associated with the problem of base exchange, or the more exact term, cation exchange. It was not until 1931 that Jenny and Brown associated the cation exchange properties of a soil with the amount and nature of its component clay minerals. (1) The development of X-ray diffraction as a research tool made it possible to study the finest fractions of clay minerals. It had been established by Hendricks and Fry in 1930 that clay material possessed an entirely crystalline structure. (2) This work makes it possible to study the identification of specific minerals in the soil.

The amount and nature of the clay content of a soil has recently come to be recognized as a major contributing factor in the total physical properties of any soil mass. The behavior of a soil, hence a foundation structure, is greatly influenced by the presence of clay minerals even if only in small quantities. Clay is the active portion or fraction of a soil. Different groups or families of the clay minerals exhibit structural characteristics and physical properties which vary markedly with their nature and environment. The engineering properties of natural soils

containing these minerals are directly influenced by them. Such properties which are of particular significance to the design or construction engineer are shear strength and stability; permeability and capacity for drainage; together with the degree of differential settlement due to consolidation under load, to name but a few.

Before extensive studies of any material are undertaken, it is first necessary to determine methods for rapid and positive identification of the material. One such method is found in the technique of X-Ray diffraction, which has been successfully used for a number of years in the field of Metallurgy. In 1951, Dearth and Williams undertook a study of the swelling characteristics of certain clay minerals by X-Ray diffraction. (3) They were concerned primarily with the development of a sound technique for the preparation of sample specimens of clay minerals for X-ray analysis. As a result of their work it was possible for the writers of this thesis to apply certain equipment and methods developed by Dearth and Williams directly to the subject of this investigation.

Heretofore, investigators have been hampered in their work by the lack of universally available clay materials which were uniform in both chemical and mineralogical composition. This difficulty has been largely overcome by the American Petroleum Institute, which is making generally available certain selected naturally occuring clay minerals. These have been arbitrarily established as standard materials for reference purposes. Accordingly, the writers of this thesis have undertaken the task of developing a series of representative X-ray diffraction patterns involving the use of standard materials obtained from the American Petroleum Institute. In this manner it is believed that a simple card file system of diffraction patterns may be prepared against which the diffraction pattern of an unknown sample may be compared for relatively accurate and speedy identification. (4). It is visualized that such a system would operate in much

the same manner as a fingerprint file, in which there is one and only one pattern for each individual.

During the early stages of preliminary work on this thesis the writers had hoped to undertake a study of the oil bearing sediments of the Wilmington Oil Field, which underly the U. S. Naval Shipyard, Long Beach, California. (5) It was soon found that largely because of the limited time available, the scope of the work would be reduced to a degree which precluded making any direct contribution to this project. Nonetheless, in view of the nature of the project as being largely a problem related to soil mechanics work, it's essential details will be related here. The project was originally conceived as a result of the rather serious problem of land subsidence in the Long Beach area which has existed since 1940, and which has every prospect of continuing until 1962. The subsidence has been attributed by many leading engineers and geologists to be directly related to the removal of oil, water and natural gas from the Wilmington Oil Field. (6) (7) One of the proposals for substantially reducing, or even stopping the subsidence is known as the "water re-pressuring method", by which it is believed that bottom hole pressures can be maintained, and further consolidation of the sediments arrested. In a report of one of the leading consulting engineering firms concerned with this problem, there is a statement to the effect that the clay minerals included in the oilfield sediments would have to be considered under a water repressuring program. It was hoped that under a program of fundamental research in clays, in which the writers are engaged, there could be learned some useful facts which could in some small way contribute to a better understanding of this problem. Accordingly, the writers contacted the Public Works Officer, U. S. Naval Shipyard, Long Beach, California for assistance in this effort.

Cdr. Bentley most generously furnished, for this use, some of the sample sediments which had been obtained from various zones and at different depths of the Wilmington Oil Field. The investigations into the identification of clay minerals by X-ray diffraction included a study of these sediments.

The writers also studied:

(a) Unknown materials which were obtained from the construction site of the New York State Thruway. These were obtained at the intersection of the thruway with U. S. Highway 9W, Albany County, New York at depths of 82 and 152 feet.

(b) Unknown refractory materials obtained in the vicinity of the Bleau Brickyard, Oil Mill Hill, Troy, N. Y., at a depth of 15 feet.

(b) Unknown materials obtained from the construction site of the new R.P.I. Dormitories on Burdette Avenue, Troy, N. Y., at a depth of 15 feet.

SECTION II

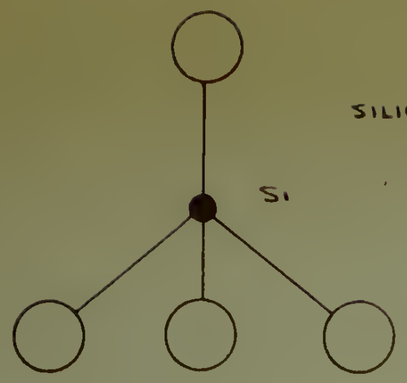
THE STRUCTURE AND CHARACTERISTICS OF CLAY MINERALS

GENERAL

The clay minerals of major importance may be classified into three main families or groups namely, Kaolinite, Montmorillonite and Illite or the Hydro-Micas. (3) The typical minerals consist of flat plate shaped particles with perfect cleavage. They are micaceous in structure. Each group contains members of essentially the same chemical composition but of quite different structural arrangement. This variation in the structural arrangement results in the formation of the different clay minerals. It can thus be shown that chemical analysis alone is not sufficient to identify these minerals. For this reason, X-Ray diffraction has come into its own as a valuable means of studying these minerals. With this method it is possible to detect changes in the structural arrangement of the different crystals including variations in the groupings of individual atoms.

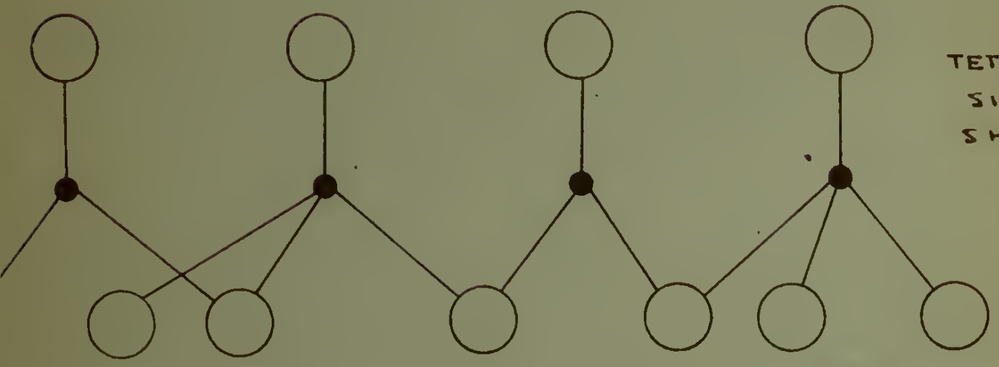
With respect to physical properties, the Kaolinite and Montmorillonite minerals represent the outer extremes of behavior, with the Illites occupying a transitional phase in between. After years of investigation and experimentation, it was concluded that the atoms or molecules of which matter is composed are arranged in symmetrical, orderly patterns. These patterns are considered repetitive and are believed to follow a set of laws whereby each fundamental combination represents a complete unit. Moreover, each such unit is considered capable of combining with other units to form a larger mass. It is these building units, both alone and in combination which comprise the space lattice.

FIG. 1



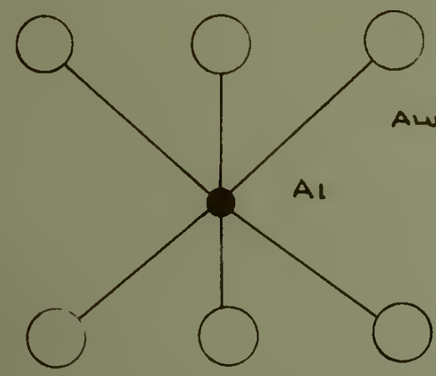
UNIT CELL

SILICON-OXYGEN TETRAHEDRON



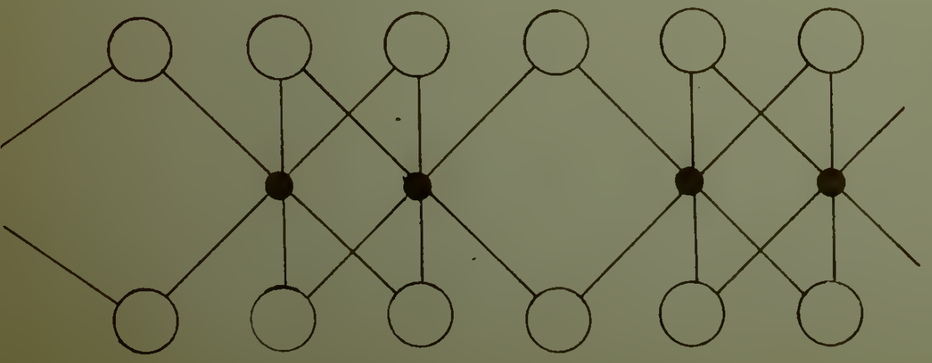
TETRAHEDRAL SILICON SHEET

FIG. 2



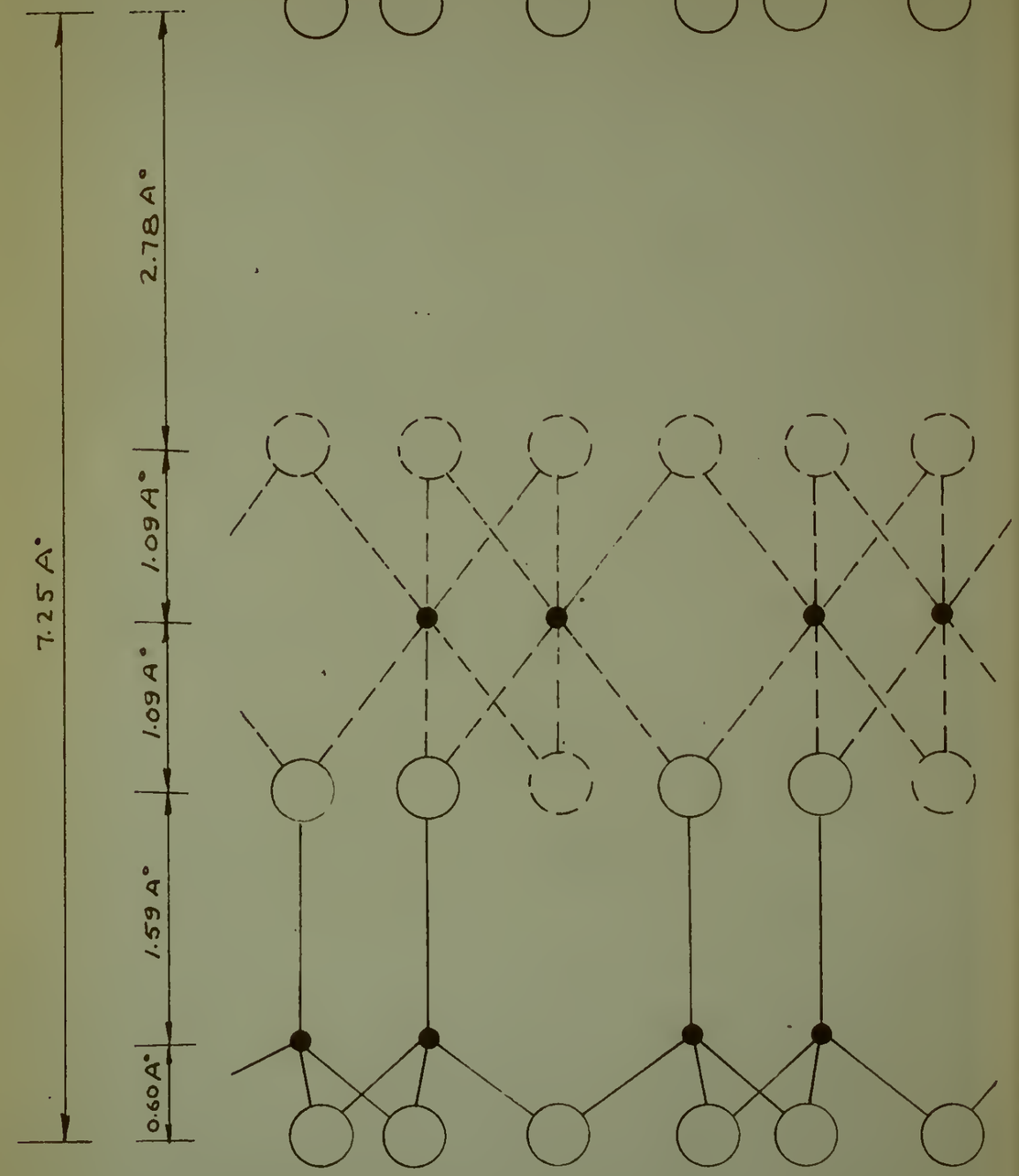
UNIT CELL

ALUMINUM HYDROXYL OCTAHEDRON



GIBBSITE SHEET

KAOLINITE LATTICE



AFTER GRUNER

FIG 3

THE SPACE LATTICE

Inasmuch as the clay minerals have been shown to be crystalline in nature, it is with this group with which we are chiefly concerned. (11) If it were possible to break down a crystal into smaller and smaller crystals of the same shape, a crystal of moleoular dimension would result. Crystalline solids are distinguished by their structural symmetry, that is, complete regularity in ths geometric arrangement of their constituent atoms and ions. It will be noted in the section of this thesis titled THEORY that an example of such a molecular unit cell is the silicon-oxygen tetrahedron (see Fig. 1) on which 4 oxygen atoms rest against each other forming a pyramidal group, with a small silicon atom in the center of the group. Inasmuch as this unit is not electrostatically neutral, it has the ability to combine in a chain-like lattice called a tetrahedral silicon sheet.

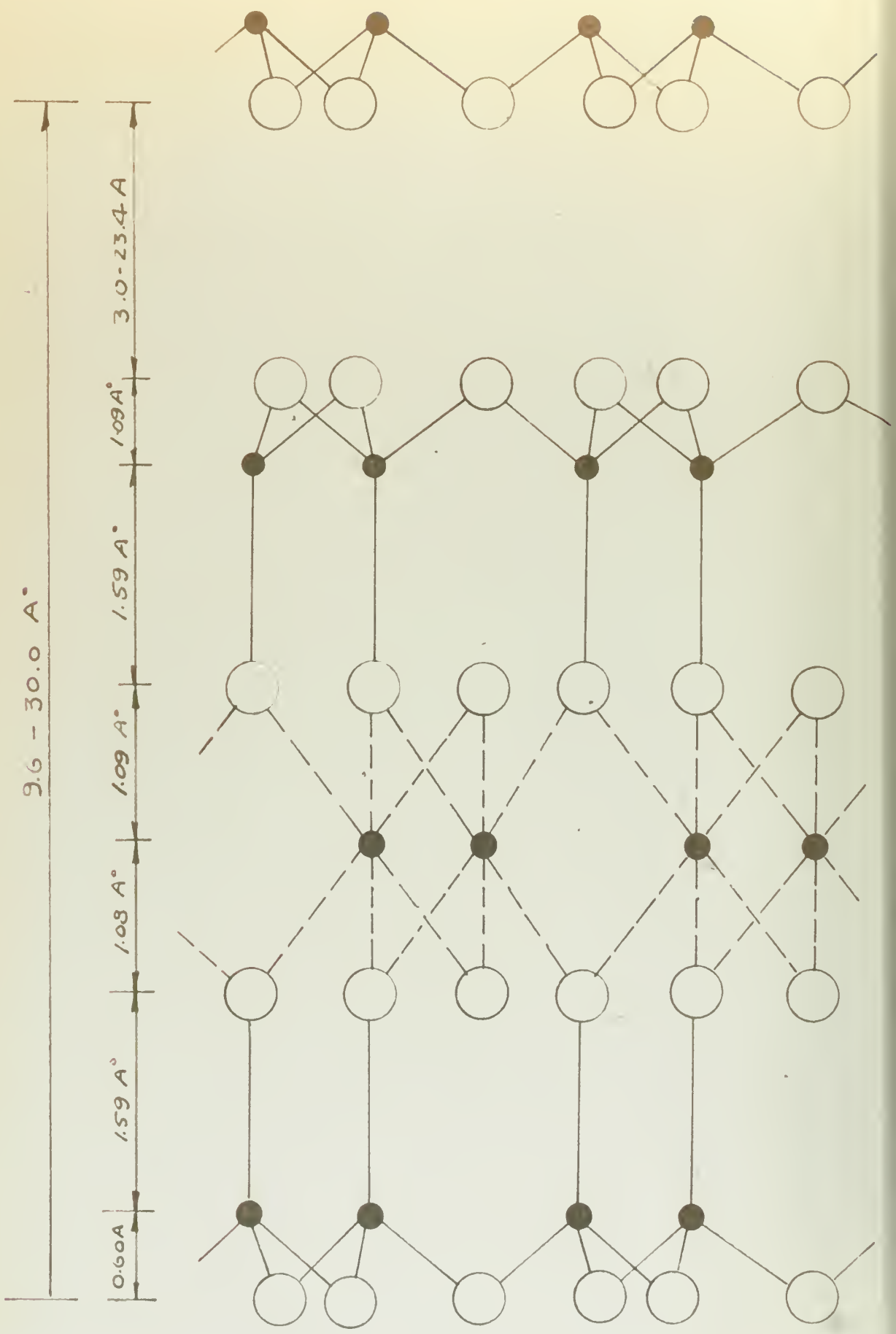
The aluminum-hydroxyl octahedron shares electrons in a similar manner, thus forming a lattice structure called a Gibbsite Sheet. (see Fig. 2) These sheets are the basic elements of the clay lattices. The different clay minerals are essentially formed through variations in the combination of these fundamental sheets together with variations in the elements present within these lattices.

KAOLINITE GROUP

Structure:

This group consists of kaolinite lattices stacked upon one another. (8) Each lattice consists of one tetrahedral and one Gibbsite Sheet linked together by covalent bonds (see Fig. 3) Such combination is sometimes called a 1:1 lattice. Strong attractive forces between the hydroxyl units on one side and the oxygen atoms on the other result in these lattices being held together tightly at the contact surfaces. Because of the strong attraction between these bonds, it is difficult for water to penetrate the lattice.

MONTMORILLONITE LATTICE



AFTER HOFMANN, ENDELL AND WILM

FIG 4

CHARACTERISTICS

(a) Interplanar Spacing: 7.2 A (10^{-8} cm) Regardless of moisture content and degree of ionic saturation.

(b) Expansion in Presence of Water: Rel. low

(c) Base Exchange Capacity: Very low (3 to 15 me/100 gr.)but increasing as particle size becomes smaller.

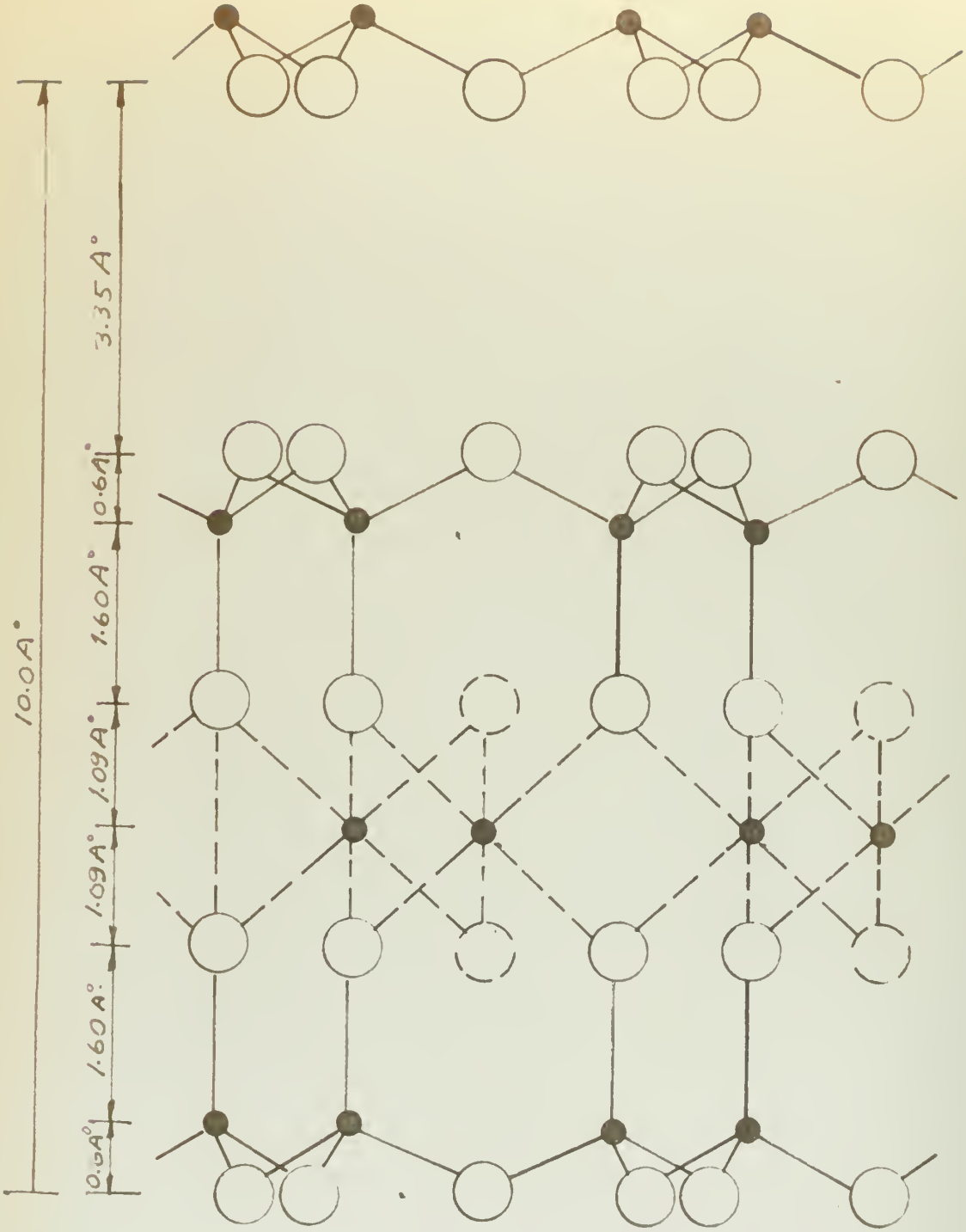
(d) Sources: Frequently found in sedimentary clays.

MONTMORILLONITE GROUP

Structure:

This group consists of the kaolinite lattice together with one additional silicon-tetrahedral sheet (see Fig. 4). It is sometimes referred to as a 2:1 lattice structure. These lattices are held together with relatively weak attractive forces because they are electrostatically balanced with oxygen atoms on both basal planes. Consequently, varying amounts of oriented water dipoles occupy the space between these lattices. This mineral is therefore considered to have an expanding lattice structure which may increase the center to center distances by more than 100%. Moreover, the loosely held condition of the lattice permits easy access by ions. These ions can readily penetrate the secondary unseparated interfaces to produce new basal cleavage planes along which the particles will tend to separate. The interplanar spacing of Montmorillonites is therefore relatively high and varying. The pronounced variations in swelling in the hydrated state is accounted for by the presence of water and hydrated ions. In the dry state, the amount of separation reflects the size of the included dehydrated ion. Montmorillonites exhibit the phenomenon of isomorphism in that replacement of aluminum by magnesium and ferric iron frequently occurs.

ILLITE LATTICE



AFTER GRIM, BRAY AND BRADLEY

FIG. 5

CHARACTERISTICS

(a) Interplanar Spacing: 9.6 to 20. A Depending on moisture content and type and amount of ionic saturation.

(b) Expansion in Presence of Water: Extremely high with volume increases in the ratio of 9 to 1 under certain conditions. The mass effect of the relatively weak lattice bonds produces a highly plastic material.

(c) Base Exchange Capacity: Extremely high, (from 60 to 100 me per 100 grams) with no material increase as particle size becomes smaller.

(d) Sources: Frequently found in the so-called Bentonite Clays formed by alteration of volcanic ash.

ILLITE GROUP

Structure

The Illite lattice is similar to that of Montmorillonite, consisting of one gibbsite sheet between two tetrahedral silicon sheets (see Fig. 5). The essential difference between the two is that about 15% of the silicon atom positions are replaced by aluminum. The resulting excess charges are satisfied chiefly by potassium ions which are located between the silicon sheets. The structural arrangement of these units is not fully understood, and the identification of Illites is therefore a difficult task.

CHARACTERISTICS

(a) Interplanar Spacing 10 to 13 A' depending on the chemical composition of the structural units.

(b) Expansion in Presence of Water Very low, resulting in a relatively constant lattice spacing over a wide range.

(c) Base Exchange Capacity Relatively 1 ow (20 to 100 me per 100 grams).

(d) Sources These minerals are reported as being the most widely distributed clay mineral in sediments accumulating on the ocean floor. Illite is the dominant mineral in most shales, and it is believed that the shaly structure is related to its presence.

FIG 6

FIG 7

FIG 8

SECTION III

APPARATUS

The following apparatus was used in connection with the work in this thesis:

(a) IONIC SATURATION EQUIPMENT

A DUMORE high speed mechanical stirring apparatus was used instead of hand stirring, to obtain maximum dispersion and ionic hydration of the sample in solution. (see Fig. 6)

An International, size 1, type C Centrifuge was used to precipitate the clay particles after complete hydration and ionic saturation had taken place. (see Fig. 7) This replaced the earlier technique of allowing the solution to stand for long periods until the suspended solid settled out. It was also used in other parts of the work where rapid filtering was required.

(b) EXTRUDING DEVICE

Powder specimens in the oven dry state were prepared with the use of an extruding device developed by Dearth and Williams in connection with their work. A photograph of this unit appears in figure 8. It consists of a cylindrical plunger, a receiver tube, and a supporting stand which were shop fabricated out of alloy steel to resist corrosion. The bottom of the receiver tube contains a .020" diameter hole thru which a mixture of powdered sample and cement are extruded in the form of a paste to form a threadlike sample specimen. The specimen is dry and ready for use in 3 minutes or less. The supporting stand portion of the assembly is used primarily to hold the receiver tube in an upright position, and to elevate the extrusion opening above the level of the working surface.

(c) X-RAY TUBE

A General Electric, type CA-6 X-ray tube with copper target was used as a source of X-rays. It consists of an evacuated tube containing two

FIG 10

X-RAY TUBE SCHEMATIC

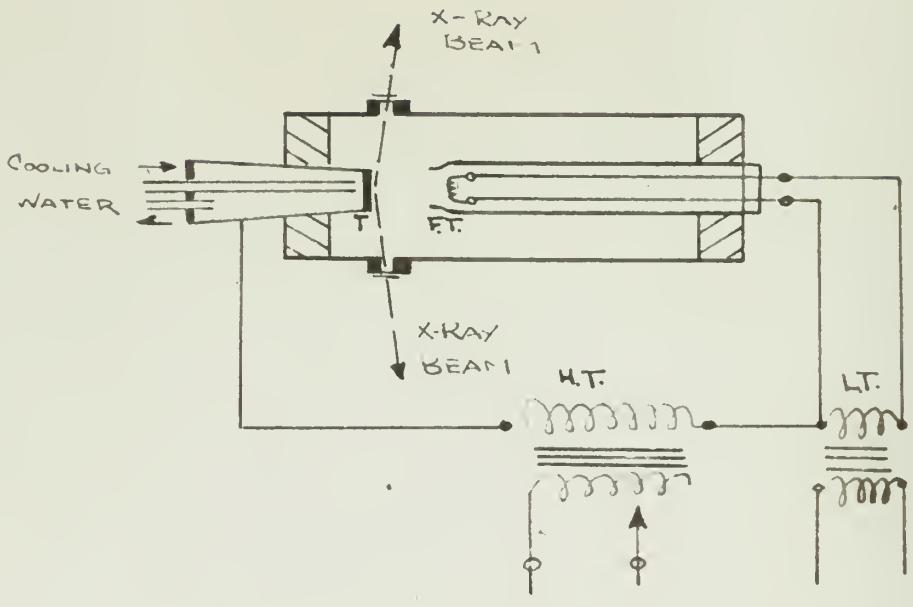


FIG. 9

electrodes. These are the cathode which acts as a source of electrons and the anode or target. A high potential difference is applied across the electrodes by means of an external power source. Under the influence of the electrostatic field thus generated, electrons leave the cathode and strike the anode with high velocity. The character of the x-rays so produced depends in part upon the speed of electron travel, and in part upon the material of which the target is made. Only a small part of the energy of the electrons is converted into x-rays upon striking the target. The major portion is converted into heat, which is commonly dissipated by means of a water cooling system. A simplified sketch of a typical tube is shown in Figure (9). Figure (10) is a photograph of the assembled x-ray generating unit used in this work.

(d) FILTERS

A nickel filter was used in this work to screen out undesirable radiation. The filter consisted merely of a thin foil of nickel about the size of a postage stamp which is placed in the direct path of the x-ray beam, across the port opening on the side of the x-ray tube. Aluminum foil was tried at first in an effort to use a more readily available material. However, it was rejected in favor of nickel because of its poor filtering qualities.

(e) EQUIPMENT PROTECTION

In the use of water cooled x-ray tubes, it is absolutely essential that a supply of circulating water be maintained. If this is not done, the tube will quickly burn out thus destroying an expensive item of equipment at a replacement cost of approximately $600. To help safeguard against such an event, a mercury switch protection device has been made a feature of the water supply service. It is nevertheless important to

Fig. 11

check the flow of water by inspection upon each use of the tube against the possibility of a faulty switch. The cooling system pressure should be maintained at approximately 20 psi, to prevent disruption of the radiation output during fluctuations in the building water supply service.

(f) PERSONNEL PROTECTION

Portable lead shields should always be carefully used to protect operating and nearby personnel from the harmful effects of scatter radiation.

(g) X-RAY DIFFRACTION CAMERAS

The Debye-Scherrer Powder Camera was used to produce the strip films for this thesis. This camera was used for about 80% of the total film work. A photograph of the Debye-Scherrer diffraction camera is shown in figure 11. This camera operates on the principle that a portion of a directed x-ray beam will be reflected from a sample specimen and recorded on a strip of x-ray film. The extruded powder sample is placed into a holder or receiver chuck in the center of the cylindrical body of the camera. The camera cover containing the x-ray films is placed in position and the assembled camera adjusted to a position in front of the x-ray tube in the direct path of the x-ray beam. The camera in position is illustrated by the photograph in Figure 10. An absolutely parallel x-ray beam is stopped with a slit, so that only an extremely thin pencil of x-ray enters the chamber. The incoming beam strikes the powder specimen, with part of the direct beam continuing on to strike the curved strip of film at producing a dark spot. The rest of the beam is diffracted or reflected to produce a cone of radiation. The concentric ring patterns on the film can be considered to be the trace of the cones

Fig. 12

Fig. 13

of radiation upon the film. In a perfectly random orientation of crystal planes, a series of perfect and well defined concentric circles will result forming a pattern which is characteristic of the material being examined Each ring corresponds to one angle of diffraction. It's properties are defined by Bragg's equation which is discussed under the section entitled Theory.

In order to examine the innermost rings more closely, and to a larger scale than is possible with the strip film (Debye-Scherrer) the cassette camera is very useful. Essentially this camera is based on the principle of using a flat film in lieu of a curved film strip. When using a flat film each diffraction is recorded as a circular diffraction halo around a central spot. A photograph of this unit is shown in Fig. 12. The cassette or flat plate camera has its greatest usefulness in precision determination of large interplanar (lattice) spacings, with correspondingly small circle diameters which are often not revealed by the strip camera. This was necessary in some, but not all of the samples used as will be explained in the PROCEDURE portion of this report.

(h) FILM

Eastman Kodak Type K film was used throughout the work

(i) DEVELOPING AND PRINTING

Standard Eastman Co. chemical solutions were used for all developing and printing.

(j) FILM MEASURING DEVICE

This equipment consists of nothing more than a vernier calibrated scale and light chamber which is used to measure the ring diameters on X-ray diffraction patterns.(See Fig. 13) With the use of Bragg's Law, the interplanar distances may then be computed with relative ease and accuracy.

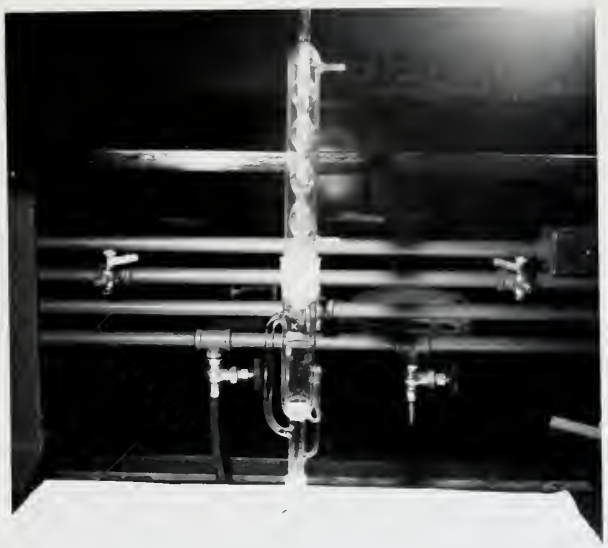


Fig 11

(11) ETHER EXTRACTION APPARATUS

A SOXHLET Ether extraction apparatus as shown in Fig. 14 was used to remove the heavy film of petroleum with which the Long Beach sediments were permeated. The equipment consists of a pyrex extraction flask, siphon tube and condenser. A sample of the sediment is placed at the bottom of the siphon tube in a pyrex thimble containing a porous glass filter in its base and ether placed in the extraction flask. Heat was supplied from a laboratory steam table at a temperature of about 150 F, which boiled the ether off into the condenser. The condensate was then returned to the flask by filtering through the sample sediment. This apparatus operates continuously, requiring only intermittent attention.

SECTION IV

THEORY

GENERAL

The study of the inner structure of matter in order to provide a better picture of the exterior form and behavior has long perplexed the world's scientists. In 1912 M. Laue, noting that the lattice of crystalline substances had a spacing between planes of several A (10^{-8} cm), theorized that X-rays whose wave length is of similar order might be used in the study of the inner structure of matter. Laue's theory was based on the diffraction of the x-ray beam from crystal faces or from planes made up of regularly spaced atoms and molecules. These planes would provide a naturally ruled three dimensional grating with just the right order of distance between rulings to ensure diffraction of the rays. Subsequent experiments proved highly successful, providing a photographic image of circles of spots produced by the diffraction beam, surrounding a central dark spot produced by the direct ray itself. In England, W. L.Bragg and his son (9, 16 and 17) were immediately aroused by Laue's discovery and accordingly set out to reduce this theory to a mere usable form. Their work resulted in a method of analysis of crystalline substances which has served as the basis of subsequent x-ray diffraction studies. In brief, the Bragg's demonstrated that x-ray patterns could be regarded as being produced by mirror like reflections of the electromagnetic waves of the x-ray beam, by regularly spaced plane sheets of atoms which make up the crystal structure. As a result of this work, it is now possible to determine the size of cells, the number of molecules per cell, the lattice type and space grouping of crystalline matter.

Prior to proceeding further in the theory of x-ray diffraction, a brief explanation will be given of the two main components of this work, namely crystal structure and x-ray waves.

CRYSTAL STRUCTURE

Practically all chemical compounds and elements exist in crystalline form characterized by their external geometrical shape. A crystal is essentially a pattern, the atoms being arranged in families or groups in such a manner that the same configuration is repeated at regular intervals in all three dimensions. The basic unit from which the pattern is created is termed the unit cell from which the overall pattern is made by stacking unit cells one on top of another. Those surfaces where the pattern has the highest concentration of atoms or ions are commonly referred to as the crystal faces or planes. When a pattern is three dimensional as found in crystalline structures, the array of points at which the pattern repeats itself is called a space lattice. The actual points themselves are termed lattice particles or points. Any plane of a crystal occupied by lattice points is referred to as a crystal or net plane. Crystal faces are always parallel to the net planes. Further, external surfaces or faces are parallel to the more densely populated net faces. Although the method of outlining the unit cell is somewhat arbitrary in practice, the choice of a unit cell for a given crystalline structure is generally determined by considerations of convenience and conformity with a symmetrical arrangement. Physical definition is accomplished by designating the lengths of edges a, b, and c and the angles between these edges α, β and γ as shown in figure 15. These edges are called unit translations in the pattern. Normally crystals have three unequal axes a, b and c enclosing angles α β and γ , which are not at right angles. However, the majority of crystals are based on a

lattice structure, which has some form of symmetry. In more detailed crystallographic study, it has been found that there are fourteen separate and distinct lattice structures. Crystallographers have also found that the slower the rate of crystallization the more perfect are the resulting crystals. Therefore, those which have attained perfect equilibrium through long periods of cooling have perfectly plane faces which meet in sharply defined edges and corners. This has special significance for the study of the structure of soils since soils are the product of the decomposition of rock, which has had infinite time to cool.

A commonly used procedure for specifying crystal faces is through the use of the MILLER INDICES, which utilizes three letters h, k and l to indicate intercepts on the x, y and z axes respectively. These indices are such that a face which is parallel to an axis has a corresponding index of zero.

X-RAYS

The discovery of x-rays in 1895 by Roentgen has had far reaching effects on many branches of science. X-rays are electromagnetic waves, which to date mean many things to many people. A better concept of wave motion can be obtained by visualizing the tossing of a stone into a pool of water from which develones ripples traveling outward in concentric circles. These waves are caused by vibrations of the water, which gradually fade out, with the resultant ripple movement becoming weaker. A wave length in this case would be the distance from the peak of one wave to the peak of the adjacent one. This distance is generally designated by the Greek letter λ . A close study of these waves would reveal that their lengths are not uniform due to the dampening effect of the waves on each other.

A uniform wave length could conceivably be produced by dropping a stone with a string attached into a pool of water and withdrawing it at equal time intervals. This would produce a wave length with no dampening effect, since a new wave would be produced each time the stone is dropped or withdrawn. Though this is a simplified explanation, it is believed that light waves, which result from the disturbance of the surrounding medium due to vibrations of particles, behave similarly. The major differences with the analogy given is that light waves travel in three dimensions. Thus, electromagnetic waves, which are similar to light waves have a wave motion of spherical extent. Depending on the length of the waves caused by different disturbances, a determination can be made of the various types of wave mechanics. Extremely long waves can be felt as warmth given off by the body emitting such waves. As the waves become shorter, they reach a range where they are actually visible. Continuing to even shorter waves, they again become invisible and cannot be felt. One of the shorter invisible wave ranges is referred to as the x-ray zone. These waves have a wave length of several A$^{\circ}$ (10^{-8} cm) and are produced by the impact of extremely fast moving electrons on a solid surface. In brief, this is the principle of the x-ray tube, where electrons are shot out from a piece of metal (cathode) on to what is termed the anticathode from which x-ray are emitted. X-ray upon striking a medium cause forced oscillation of the obital electrons of the atoms which they traverse. These electrons absorb energy from the x-rays when moving away from the nucleus and radiate energy in all directions when moving toward the nucleus.

BOMBARDMENT OF CRYSTAL FACES WITH X-RAYS

To obtain deflection from a wave striking a surface, it is necessary to have discontinuities or irregularities on the surface of the deflecting medium of approximately the same order as that of the deflected wave.

FIG 16

In the case of X-rays where the wave length is extremely short, these irregularities must be quite small. Fortunately, nature provides an ideal medium in crystal structures to conduct such studies.

A somewhat simplified version of the phenomenon of the bombardment of a crystal with x-rays is shown in figure 16. Lines 1, 2, 3 and 4 correspond to the lattice planes, at which points the pattern of the arrangement of atoms or ions is repeated. Let it be assumed that a parallel beam of x-rays, A, B and C enter the crystal from the left. To further clarify the diagram, wavy lines are superimposed over the dotted lines to show the wave length of the x-ray beam. Ray A of this beam first strikes the crystal plane at point Z and is partially deflected to the right along the path L; the remainder of the ray passes through the first plane and is partially reflected by the second plane along path M in a direction parallel to the reflection of the first and then passes through successive remaining planes as shown. To simplify the sketch, the reflection of the lower two rays upon striking the first plane at points X and Y have been omitted. That portion of ray B which has not been reflected at point Y will strike plane 2 at point W and be reflected as shown by the dotted wavy line along path L. Continuing to plane 3, ray B strikes the plane at point V and is reflected in the direction of M. Referring to the law of optics (18) it will be observed that the wave length selected is such that the distance between planes corresponds to one-half of a wave length. In this instance, Ray B, upon reaching point W and being partially reflected, reinforces the portion of ray A reflected at point Z. If a wave length had been selected to say one-third of the distance between planes, it is easy to see that the effect would be that of the various waves counteracting rather than reinforcing each other. Thus it is seen that reinforcement is only possible

if distance ZW corresponds to one wave length or some multiple thereof. It may be stated that YW is equivalent to $n\lambda$, where n is a positive interger. This statement can be further simplified by replacing the distance ZW with the angle of incidence θ, and the distance d between planes as shown in figure 17. In the triangle ZWV, $\frac{ZW}{ZV} = \sin \theta$. Since $ZW = n\lambda$, ZV must be equal to 2d. Thus, from this data can be written the fundamental law of reflection: $n\lambda = 2d \sin \theta$. This equation as developed by the Bragg's (16) gave a practical solution to the x-ray diffraction problem. It can be seen that the formation of pencils of light, resulting from reinforced rays, is premised on the existence of equally spaced planes in phase with the wave length of the x-ray beam.

DATA OBTAINED FROM X-RAY DIFFRACTION STUDIES

Information obtained by directing an X-ray beam at a crystalline substance enabled the calculation of the location of atoms which make up the unit cell (space grouping of the smallest number of atoms making up a complete crystal structure). The theory as originally developed by Laue necessitated the use of well grown and developed crystals, which made X-ray diffraction methods of little value for the colloidal physicist. As a result P. Debye and P. Sherer (9 and 17) developed a method of X-ray diffraction study for substances available only in powder form. The reasoning used was that if a crystal is ground to a fine powder, it can be assumed that a mass of this powder will have crystal faces present in absolute random orientations. Thus, if a powder specimen is subjected to an X-ray beam, it is to be expected that the multitude of lattice planes will lie in all of the angles called for by the deflection equation producing halo or conical pencils of light. The position of these cones are recorded on film placed perpendicular to the cone axis. These

FIG 18

diffraction lines or rings as shown in figure 18 represent all families of planes in the crystal and are normally referred to as powder patterns. From this discussion, it is apparent that crystal structures with definitely fixed distances between planes will produce identical x-ray patterns.

On the other hand, if the distance between planes is maintained, but the distance between atom centers within individual plane surfaces is varied, the diffraction pattern will either expand or contract. However, if the space arrangement is altered, the diffraction pattern is changed. Upon examining x-ray diffraction patterns, it will be observed that the lines have varying intensities depending on the angles at which the reflection occurs, the number and arrangement of atoms in the lattice, perfection of the crystal irradiated by the x-ray beam and methods employed in photographing the crystal. It may, therefore, be stated that X-ray patterns serve as fingerprints of the various crystalline substances. Actually, this pattern represents a summation of all of the components of the crystal. Further, the intensities of the lines revealing variations in arrangement of atoms is an indication of the relative quantities of matter present in the crystal. (9, 10, 15, 16 and 17).

It has been found that if a constituent is present to an extent less than ten percent, the lines may be completely obscured by those substances present in larger quantities. (10) In short, the entire art of crystal analysis revolves around the determination of the atomic arrangement, which for other than general observations is far too complicated to be included in this investigation.

STUDY OF CLAY MINERALS BY X-RAY ANALYSIS

Certain repetition of material covered in the section entitled Structure and Characteristics of Clay Minerals will be noted, however, in the interest of continuity, such duplication appears justified.

The clay minerals have had infinite time to establish complete equilibrium in nature and are, therefore, ideally adapted to X-ray diffraction analysis. Though some qualitative work has been performed in this field relatively little quantitative work has been accomplished to date. The clay minerals have a layer lattice type structure, which is micaeous or platy in appearance. The small thin sheets are irregular in shape and in general have perfect cleavage. The principal components of the various lattices of the clay mineral are the covalent silica-oxygen tetrahedron and the alumino-hydroxyl octahedron unit cells discussed in more detail elsewhere in this report. These unit cells form sheets called the Gibbsite and tetrahedral sheets, which are bound together by electrostatic forces.

X-ray patterns of clay reveal two separate series of lines. (10) The first is due to the two dimensional crystallites (indices h, k and l). The second results from a single series of orders, indexed 001 (the crystal plane being perpendicular to the xy plane) due to the intersheet separation. The latter series of lines are the ones that are of primary concern to the soil investigator. Changes due to adsorption are shown in the second case only. These lines or pencils of light clearly indicate any expanding lattice tendencies of the clay mineral. They also provide information relative to the nature and number of cations absorbed on the surface of the lattices and the quantity of water present. (2, 10, 13 and 14) An expanding lattice is quite pronounced in Montmorillonites, but hardly preceptible in Kaolinites. The structural arrangement of the Montmorillonite, where a gibbsite sheet is held between two tetrahedral sheets with oxygen bonds on the outer layers of both sheets results in weak attractive forces between the layers or planes. On the other hand, Kaolinite consists of a single gibbsite and tetrahedral sheet with hydroxyl bonds on one side and oxygen on the other with a resultant strong attractive force.

In the actual application of X-ray diffraction techniques to the identification of clay minerals, the interpretation of the various diffraction patterns requires computation of the interplanar spacing (distance between sheets or planes). From the computed spacings, a comparison can be made with some known standard such as Hannawalt's (10 and 15) or with results obtained by other investigators from known clay mineral samples. In addition, a comparison of relative intensities of the lines of the individual patterns provides information concerning the amount of the various components making up the clay mineral. Thus, the method of X-ray diffraction has quantitative as well as qualitative aspects.

SECTION V

PROCEDURE

GENERAL

Bedford, Indiana Halloysite (h-12); Macon, Georgia Kaolinite (H-4); Morris, Illinois Illite (H-36); Pioche, Nevada Montmorillonite, Gouge Clay (H-32) and Otay, California Montmorillonite, Bentonite (H-24) were selected as being representative of the overall field of clay minerals. For ionic saturation of these clays, it was decided to use Hydrogen, Sodium, Potassium and Calcium since these have been used by the majority of previous investigators and are commonly found on clay particles in nature. Hereinafter the chemical symbols for these elements will be used.

Inasmuch as the expansion or swelling characteristics of the various clay minerals is a major consideration in engineering work, specimens of each mineral were prepared with various ionic saturation. Both oven dry and hydrated forms were used. Oven dry samples were heated for twenty four hours at 110°C. Hydrated samples were mixed with distilled water in a high speed stirrer for 20 minutes. The experience of previous investigators (3, 9 and 10) indicated that the sharpest diffraction patterns were obtained by using particles passing a 200 mesh sieve. This was used as an initial starting point in the determination of the most desirable particle size. Subsequent tests indicated that particles appreciably larger than this size would produce spots rather than rings on the diffraction pattern. Though the investigations were inconclusive, it appeared that particles smaller than those passing a 325 mesh sieve would also give a poor pattern. It was therefore concluded that material passing a 200 mesh sieve is, in general, satisfactory for all minerals except the Illites, where spotty or grainy patterns were obtained with this size. Time and equipment limitations pre-

cluded further study along this line. Therefore, as a preliminary step, all samples were ground with a mortar and pestle until they passed a 200 mesh sieve after which they were dried in an oven for twenty four hours at a temperature of 110°C.

HOMO-IONIC SATURATION

Peptizing the clay minerals was accomplished by following the procedure adopted by the International Society of Soil Sciences (11). Four grams of the material passing a 200 mesh sieve were boiled for five minutes in thirty cubic centimeters (cc's) of six percent hydrogen peroxide. This treatment was intended to remove organic material which might have been retained on the particles and which would have effected subsequent diffraction patterns. The residual hydrogen peroxide was removed by centrifuging and piping off the supernatant. In order to leach out those monovalent or divalent ions, which frequently occur on the particle surface in nature, the sample was treated with twenty cc's of 0.17 normal hydrochloric acid. Strongly held hydrogen ions of the hydrochloric acid replaced the originally held ions giving a hydrogen saturated clay, as shown in the following:

$$\text{CLAY}\Big)\begin{matrix}\text{Ca}\\ \text{Mg}\end{matrix} \xrightarrow[\text{leached and washed}]{\text{HCL}} \begin{matrix}\text{H}\\ \text{H}\end{matrix}\Big(\text{CLAY}$$

The HCL saturated mixture was centrifuged and the remaining liquid poured off. In order to correlate this investigation with other published reports with regard to the completeness of ionization as related to the pH value, a pH reading was taken of the HCL supernatant using a standard Beckman pH meter. Hosking (12) has conducted a study relating pH values to the degree of cation exchange and has concluded that the maximum cation exchange capacity is attained with a pH value of 9.0. He further reported that the material has a minimum ion content with pH values as low as 5.0 and that the degree of

saturation rapidly diminishes beyond a pH of 9.0. It might be stated that other investigators have found that maximum ionic saturation is achieved with pH values ranging from 8.4, Bradfield and Allison (1933), to 10.0 or 11.0, Hissiak (1924) and Page (1926). In view of these differences it was determined impractical to adjust the pH values to any predetermined value. The sample was then washed three times with distilled water in order to remove the dissolved carbonates and the replaced ions. At this point, the four gram sample was equally subdivided into four individual flasks. One of the flasks was labeled _____ mineral, hydrogen saturated. The remaining three subdivisions were peptized with Na, K and C ions utilizing the following procedure. Approximately thirty cc. respectively of 0.008 normal sodium hydroxide, potassium hydroxide and calcium hydroxide was added to three flasks containing approximately one gram of hydrogen saturated sample. This mixture was beat for twenty minutes in a high speed stirrer after which it was centrifuged and the supernatant withdrawn. The fourth flask contained the previously prepared sample treated with H ions. A pH reading was made of the residual base resulting from the centrifuging process. The four samples were then each divided into two categories; one to be dried in an oven for twenty four hours at 110 °C and the second to be hydrated by mixing the sample with distilled water in a high speed stirrer for twenty minutes. The hydrated samples were placed in a test tube to develop maximum hydration and for convenient storage prior to being prepared for X-ray diffraction. This enabled X-ray studies to be made of oven dried and hydrated specimens of Halloysite, Kaolinite, Illite, Montmorillonite, Gouge Clay and Montmorillonite, Bentonite, each being saturated with H, NA, K and Ca ions. In addition specimens were prepared of all five minerals in their original or as received condition in both an oven dry and hydrated state.

PROCESSING SAMPLE FOR PHOTOGRAPHING WITH X-RAYS

Inasmuch as the primary purpose of this investigation was to study the diffraction pattern of various minerals as distinct from establishing procedures; the techniques employed by previous investigators were initially employed. Consequently, the optimum thickness of specimen for exposure to the X-ray beam as recommended by Dearth and Williams and others (9 and 10) was accepted. Their study revealed that from the relationship $t = 2/\mu$, where μ is the linear adsorption coefficient and is equal to $d \sum p(\mu/p)$, that a thickness of 0.20 mm. is most effective. Subsequent experiments with both smaller and larger thickness of sample appeared to have little or no effect on the final results. Previous investigators have found that the size of specimen has its greatest significance in studying materials with high atomic weights. Reports of previous workers in X-ray diffraction (9, 10, 11, 13 and 14) were reviewed to determine the most effective method of mounting the specimen in the camera chuck holder. These papers indicated that glass tubes, cellophane tubes, various types of plastic tubes, preparation of specimen between glass slides and a method of extruding the sample into a thread had all been used. Since the extrusion procedure appeared simple, provided acceptable patterns and the device was available, it was decided to use this procedure for the first few exposures. Essentially this method consists of mixing the fine clay mineral powder into a stiff paste using household Duco cement or some other suitable binding material and extruding the material through an extruding devide (see APPARATUS) into a cylindrical thread. Experiments with various binding materials suggested that collodion was more effective than Duco cement in that it is initially more fluid and has a much more rapid rate of hardening. An alternate method was also tried consisting of filling small plastic tubes with the dry powder by sticking the tube into

the powder and then packing it with a wire rammer. Whereas, the results were satisfactory, this technique did not provide as sharp a pattern as obtained with the extruded threads. This was undoubtedly due to the reduction in the reinforcement of random orientations of the crystal faces. In addition, this latter method was found to be extremely tedious and time consuming. The method employed by many metallurgists of using cellophane tubes into which the powder is packed was rejected for the same reasons. Informal discussions with metallurgists suggested that they do not find this method entirely satisfactory and are attempting to develop a better procedure. The extrusion method was, therefore, used for preparation of all oven dry specimens.

While the extrusion method was adapted to dried samples, it could not be used for the hydrated samples where contact with air would cause the sample to lose much of the loosely held water. Therefore, a method had to be devised which would insure the specimens remaining completely hydrated throughout the entire period of exposure to the X-ray beam. This problem was given considerable thought and as an initial step, hydrated specimens were extruded using no binder except the water of hydration. After extrusion, the specimens were dipped in collodion in order to seal the sample. It was found, however, that the drying process of the collodion removed a considerable amount of the water from the sample. As another possibility, small diameter,(approximately .0200")glass tubes were drawn. The tubes were filled with the hydrated slurry by utilizing the capillary tendencies of the hydrated material. It was found that the slurry would rise to a height of approximately one inch. Once the tubes were filled, they were sealed at both ends with collodion. This procedure proved to be technically satisfactory; however, the exposure time was doubled over that required by

other methods. It is believed that this increase was due to the thickness of the walls of the tube and the high X-ray adsorption characteristics of glass. An improved method of drawing the tubes, so as to get extremely thin walls would undoubtedly prove this procedure satisfactory. The method employed by Dearth and Williams was next imvestigated. In brief, this procedure is one of coating annealed copper wire with a plastic material made from ethyl cellulose dissolved in methyl ethyl ketone and xylol. Upon being thoroughly dried in an oven at 50 C, the plastic coat or tube can be removed by stretching the wire at its ends, thus reducing its diameter and causing the wire to separate from the plastic material. Numerous experiments were tried with various wire sizes and although better definition was obtained with larger tubes due to the larger number of random orientations and greater strength achieved, it was necessary to adhere to the optimum size specimen referred to in connection with the oven dried specimens, in order to reduce distortion. Tubes 0.025 inches in diameter were finally selected as most satisfactorily meeting all requirements. In attempting to arrive at the most efficient coating procedure, it was found that a single coat was inadequate and that too many coats would result in the tube wall being too thick. It was finally determined that the best procedure was to dip the tube, hang it vertically for approximately ten minutes and then dip the wire a second time. The coated wire was then placed in the oven. Various drying times and temperatures were tried. In so far as temperature is concerned, it is believed that the temperature used by Dearth and Williams of 50 C is the most desirable; however, it was found that little difference could be noted whether the tubes were dried for twelve or forty-eight hours. The technique finally adopted was to cut the wires into two inch lengths, since tubes approximately one and one-half inches long were required, double dip the wires and allow twelve hours drying time. Using this procedure

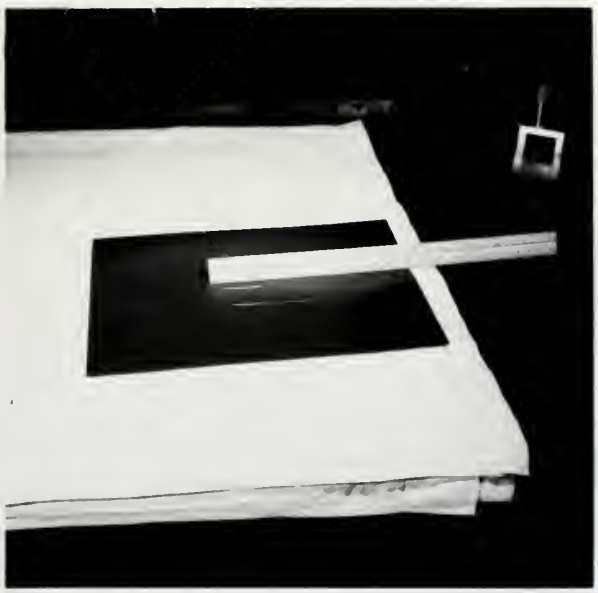
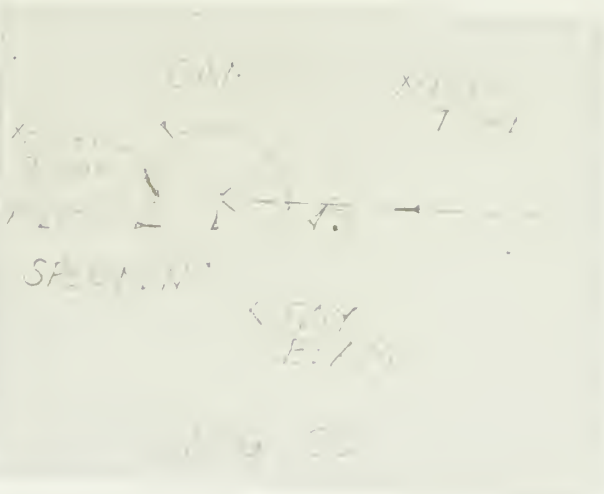


Fig. 19



tubes were made up in lots of twelve to fifteen at a time after which they were stored until required. A photograph of one of these tubes is shown in figure 19.

These tubes were filled by pipetting approximately two cc's of the hydrated sample into a shallow dish, which was allowed to air dry for approximately one hour to permit the top layer of water to evaporate off. The plastic tube with its original wire in a loosened condition on the inside was inserted into the slurry and the slurry slowly pulled into the tube by gradually withdrawing the wire. This created a vacuum sucking the slurry in behind the withdrawing wire. The plastic tube was then sealed at both ends with collodion. After being allowed to dry for approximately twenty minutes, the filled tube was placed into a test tube filled with distilled water. This enabled mass production filling of the tubes and their subsequent storage until required. Investigations of tubes stored in this manner for several weeks revealed that the hydrated material remained in perfect condition.

PROCEDURE FOR PHOTOGRAPHING THE SOIL SPECIMENS

The extruded oven dried threads and hydrated plastic tubes specimens were both photographed in a Debye-Sherrer powder camera by placing the specimen in a chuck holder as shown in figure 20. Previous investigators have found that the Kodak, type K, X-ray film gave the best definition of lines at a relatively fast rate. The X-ray tube used is referred to as a copper X-ray tube. More specifically this means that the tube uses the α line of the K series of copper for radiating the X-ray beam. For investigations involving larger spacings, molybdenum tubes would probably be superior; however, equipment availability and time considerations made it appear desirable to use other means described later in this report.

A nickel filter was used to exclude from the directed beam, those X-rays which are longer than the interplanar distance of the clay minerals. With a copper tube and nickel filter, it was found that the exposure time varied between three to six hours depending on the distance of the specimen from the X-ray tube.

In photographing clay minerals with large interplanar spacings (distance between planes) the Debye-Sherrer powder camera and copper X-ray tube combination was found inadequate since the innermost rings, resulted from the largest spacing. Consequently, these innermost rings appeared in that region on the film, opposite the collimation spindle, where the hole was punched or where the central portion of the film was shielded by the X-ray trap. The solution of this problem involved two steps; first, the use of a flat cassette camera (see APPARATUS), which did not have an obliterated central area; and second, an increase of the distance from specimen to film from 2.85 cm. to 6.0 cm. This modification in technique proved to be satisfactory to photograph the inner ring. However, the flat cassette procedure does not give circles of large radius (small interplanar spacing) and the definition was in general poor. Consequently, for those minerals with large interplanar spacings, namely Montmorillonites and certain Illites, the two procedures were used together. The cassette camera was used to photograph the innermost ring only and to cross-check the smaller rings photographed with the Debye-Sherrer camera. As a matter of routine all of the clay minerals studied were photographed with both cameras; however, it was found that only the aforementioned clay families had small inner rings.

In developing the resulting diffraction patterns, standard dark room procedures were used. The film was developed for seven minutes in

standard developing solution, washed for one minute, fixed in a standard fixing solution for sixteen minutes, washed for twenty minutes and then allowed to dry. These times are somewhat flexible and should be varied depending on the strength of the solutions used.

ADDITIONAL SAMPLES

In addition to the aforementioned samples, identification tests were run on the following samples referred to in the INTRODUCTION:

(a) two samples from the Corning Hill area intersection New York Thruway and U. S. Route 9W, Albany County, New York, (one at a depth of eighty two feet and one from a depth of one hundred fifty two feet);

(b) one sample of refractory clay (Bleau Brickyard) from Oil Mill Hill area, Troy, New York (depth of fifteen feet); and

(c) one from the newly constructed R.P.I. dormitories on Burdette Avenue, Troy, New York (depth of fifteen feet).

These samples were prepared and photographed in the same manner as that described for the five known clay minerals, in both an oven dried and hydrated "as received" condition. Although homo-ionic saturation would undoubtedly provide additional information on these unknown clay minerals, it was considered that such procedure was not necessary in simple identification.

Further, as a supplement to this study, an attempt was made to identify the clay fraction in the oil bearing sands underlying the Long Beach Shipyard area, Long Beach, California. These samples as received were coated with oil, necessitating some means of removal of this oil before specimens could be prepared and photographed. It was by no means certain that even if the specimen could be prepared with the oil surrounding the particles that the results would not be seriously effected. Accordingly, various schemes were employed to remove the oil; initially the samples were

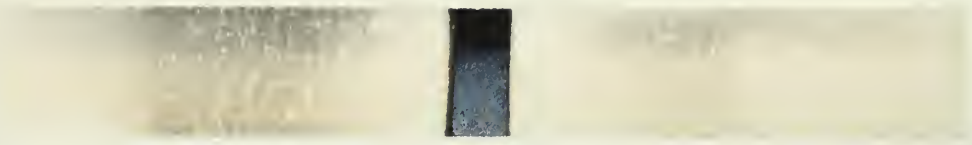


FIG 21

FIG 22

repeatedly washed with acetone. It was found that this procedure removed only a portion of the oil at best.

An ether extraction apparatus (see APPARATUS) which is commonly used in determining the oil content of soils was then tried. Several samples were placed in this device and the ether permitted to alternately evaporate and condense, thus washing the material for an eight hour period, after which it appeared that all or most of the oil had been removed. These samples were sieved and specimens prepared for photographing in accordance with the previously described procedure. The patterns so produced contained large spots in more or less ring patterns rather than the distinct rings obtained from clay minerals, see figure 21. This immediately suggested two problems, namely that the specimens contained a large quantity of quartz crystals and second that the particles were too large. Accordingly the sample was sieved in a 325 mesh screen and specimens prepared. The patterns of the specimens photographed from this finer material also had a spotty appearance, as shown in figure 22. It was then decided that the spots were due to a predominance of quartz crystals and that possibly a procedure could be developed to separate the colloidal fraction from the sample. Two separate methods were tried in an attempt to accomplish this separation (11).

First, a sedimentation process was used wherein the sample was dropped into a tall beaker of water to allow the coarse quartz material to fall out while the smaller colloidal particles remained in suspension. When the larger quartz particles had fallen below a predetermined level in the beaker, the finer material above this point was pipetted off in solution. This colloidal solution was evaporated, but unfortunately the quantity of colloidal material retained was so small as to be of no value.

Another procedure used was to make up a solor solution of material passing the 325 mesh sieve, which was centrifuged to obtain stratifications

Fig 23

SAMPLE CALCULATIONS

[illegible] SLIDE CAMERA

FLAT CASSETTE CAMERA

of the material. Visual inspection indicated that only the topmost layer consisted of nongranular material. This layer was carefully removed; however, the quantity received proved to be too small to be of use. Accordingly, no further X-ray diffraction work could be accomplished with these samples, since the clay content was too small for the removal of a sufficient quantity to be photographed with the equipment available. In order to add further confirmation to this finding a specimen was given a differential thermal analysis. This test indicated a minimum amount of clay mineral. A geological study of the granular material indicated that the primary constituents appear to be quartz, mica and unweathered feldspars. It can be surmised that the samples were depleted of the major part of their originally contained clay through oil pumping operations. Moreover, the normal handling of the samples in preparing them for this investigation undoubtedly resulted in a loss of some of the clay material.

READING THE DIFFRACTION PATTERN AND COMPUTING THE INTERPLANAR SPACING

The radii of all visible rings on the film from both the Debye-Sherrer and Cassette type cameras were read by using the measuring device described under APPARATUS. Computations were then made using the Bragg's law discussed under THEORY, as shown in figure 23.

INTERPRETATION OF DIFFRACTION PATTERNS

The interplanar spacing for all visible rings were computed and recorded together with the relative intensity of each ring as determined by visual comparison. The most intense ring had a relative intensity of one, the second most intense two, etc. Through the combination of actual photograph of the diffraction patterns the interplanar spacings and relative intensities, a finger print is obtained of the specific type of clay mineral. By taking a pattern of an unknown clay mineral with its computed interplanar spacings, an identification can be made by comparison with known patterns and spacings.

Another method used in this investigation was to relate the results.

obtained with standard ASTM cards of certain of the clay minerals. Normally in this procedure, which is known as the Hannawalt Method, (10 and 15) only the interplanar spacings of the three most intense lines are used. It was found that the rather rough method used in determining relative intensities, together with the similarity of intensity of certain of the brighter lines makes this method somewhat difficult. Therefore, greater reliance had to be made on the interplanar spacings with subsequent correlation of relative intensities.

POSITIVE PRINTS OF PATTERNS

Positive contact prints of all diffraction patterns were made on glossy printing paper using standard photographic printing procedures. It is desired to emphasize that the contact prints reveal considerably less data than shown on the negative. Consequently, only the negative is used for computation work.

SECTION VI

RESULTS AND CONCLUSIONS

STANDARD X-RAY DIFFRACTION PATTERNS

Interpretation of the diffraction patterns obtained from exposure of clay mineral specimens to an X-ray beam was limited to an analysis of the maximum interplanar spacings of the planes or faces making up the crystal structure of the clay minerals. A tabulation of all interplanar spacings found in the five samples examined is given in APPENDIX A. A study of the smaller interplanar spacings requires an extensive knowledge of crystallography, which is beyond the scope of this thesis. Each of the five clay minerals will be considered individually in the following paragraph with respect to relative interplanar spacing and various types of homo-ionic saturation. Both oven dried and hydrated forms will be discussed and a correlation will be made of the results obtained with the degree of homo-ionic saturation as reflected by the pH readings.

In strict accordance with cationic radius, the interplanar spacing of the clay minerals should theoretically adhere to the following sequence (11).

(a) Oven Dried - Ca > K > Na H?

(b) Hydrated - Na > K > Ca H?

Prior to discussing the significance of this theoretical data, it may be well to list some of the inaccuracies, which enter into X-ray diffraction work:

(1) Variations in the degree of homo-ionic saturation as reflected by the pH meter.

(2) Distortions due to specimens not being exactly centered in the camera in all orientations.

(3) Unknown moisture content of both dry and hydrated specimen.

(4) Discrepancies in reading the diffraction ring diameter - this is primarily due to failure to measure the exact center of the band or ring. (An error of one millimeter will result in a difference in interplanar spacing of 0.08 A).

(5) Error in measuring the exact distance from the center of the specimen to the plane of the film in the cassette exposures.

(6) Film shrinkage.

(7) Human errors in computing interplanar spacings.

HALLOYSITE

Relative Interplanar Spacings: Oven Dried Na > K > H > Ca

Hydrated K > Na > Ca > H

Net change between corresponding oven dried and hydrated specimens due to swelling: K(0.22 A) > Ca(0.18 A) > Na (0) H (0)

pH values of peptized clay solution:

HCL (1.5); NaOH (10.5); KOH (6.8); CaOH (8.7)

KAOLINITE

Relative Interplanar Spacings: Oven Dried Na > H > Ca > K

Hydrated Na > Ca > H > K

Net change due to swelling: Na(0.29 A) > H(0.18 A) > Ca(0.04 A) > K(0.02 A)

pH values of peptized clay solution: HCL (0.75); NaOH (10.5); KOH (9.5); CaOH (9.0)

An analysis of the Halloysite and Kaolinite, both members of the Kaolinite family, reveals that the maximum swelling that could possibly have taken place would be 0.22 A for the Halloysite and 0.29 A for the Kaolinite. Inasmuch as the Kaolinite family is normally considered to have no swelling characteristics regardless of the amount and kind of cations or water content, (19), it is believed that these minor differences in interplanar spacings are due to errors discussed in the preceding paragraph. It is, therefore, concluded that the diffraction patterns of the Kaolinite family show an interplanar spacing of approximately 7.2 A and that the results obtained are substantially correct.

ILLITE

Relative interplanar spacings: Oven Dried: Na > K > H > Ca

Hydrated: Na > H > K > Ca

Net change due to swelling: H(1.25 A) > K(0.72 A) > Na (0.35 A) > Ca(0.38 A)

pH values of peptized clay solution: HCL(1.20); NaOH (4.8); KOH (4.5); CaOH (4.9)

A review of the diffraction patterns of the Illite sample indicates a limited degree of swelling which is contrary to the results of previous investigators (21) who report that the Illites have no or extremely little swelling. Further investigators have for some time held that the widest spacings of Illite isapproximately 10 A (11). This immediately suggests the presence in the Illite sample of a small quantity of some type of clay mineral possessing an expanding lattice. It is, therefore, concluded that this sample includes a small quantity of Montmorillonite. The statement regarding the quantity of Montmorillonite is based on the relatively small amount of swelling compared to the considerable swelling found in

relatively pure Montmorillonites (11 and 24). A comparison of the relative degree of swelling with respect to the homo-ionic saturation is difficult to make. First, the pH values indicate only a partial saturation of the Na, K and Ca cations and second, the small differences found in the interplanar spacings may be partially due to discrepancies referred to previously. It does, however, appear that the Illite sample in its "as received" condition contained a high concentration of H ions, which were not completely replaced by the Na, K and Ca cations. Hence, the relative variations in the interplanar spacings would reflect the presence of the H as well as other partially saturated ions. In conclusion, it may be stated that Illites are poorly adapted to X-ray diffraction procedure. This finding was confirmed by Hellman, Aldrich and Jackson (20), and Barshad (23).

MONTMORILLONITE, GOUGE CLAY

Relative interplanar spacings: Oven Dried Ca > Na > H > K

Hydrated H > Na > K > Ca

Net change due to swelling: K(3.47 A°) > H(2.96 A°) > Na(1.32 A°) > Ca(.03 A°)

pH values of pentized clay solution: HCL(3.2); NaOH (10.8); KOH(9.0); CaOH(9.0)

The relative interplanar spacings of the oven dried samples saturated with the various ions shown above appear to be relatively consistent with the theoretical spacings given in the first paragraph of this section. The increases in the interplanar spacing brought on by the increased diameters of the hydrated ions follows the sequence that would normally be expected for a clay mineral with an expanding lattice. It might be noted that the pH values of the pentizing agents in this case are in accord with the results of Hosking (12) and, therefore, indicates

complete homo-ionic saturation of the clay mineral.

MONTMORILLONITE BENTONITE

Relative interplanar spacings: Oven Dried H > K > Na > Ca

Hydrated K > H > Ca > Na

Net changes due to swelling: K(7.27 A°) > Ca(6.23 A°) > H(2.81 A°)

Na(2.18 A°)

pH values of Peptized clay solution: HCL(0.9); NaOH(3.6); KOH(3.8);

CaOH(3.6)

Prior to discussing the relative interplanar distances of the various homo-ionic saturated specimens, it is desired to emphasize the extreme acidic pH value of the H saturated Bentonite. This strongly suggests that this clay was highly saturated with hydrogen ions in nature. Further, it will be observed that the alkalinity of the peptized clay solution is far under that reported by Hosking, which indicates that the degree of homo-ionic saturation is considerably less than maximum. This phenomenon can be explained by the inability of the basic ions to completely replace all of the hydrogen ions. It is, therefore, to be expected that the interplanar spacings will be erratic. In the oven dried patterns, the smallest spacing was found in the calcium saturated specimen which suggests that relatively few calcium ions are attached to the clay particles. This observation will be further substantiated in the case of the hydrated calcium specimen. The hydrated spacings further bear out the limited degree of ionic saturation. It will be noted that the potassium clay has the widest interplanar spacing. This would normally be considered to be contrary to any theoretical expectations. However, as mentioned previously, these specimens all undoubtedly had a considerable quantity of hydrogen ions on the surface and a corresponding limited number of basic ones. Further

Baver (11) states that "there is a decreased swelling as the K ions in the system increases". It is therefore concluded that the large number of H ions coupled with the increased swelling of the small number of K ions accounts for the large interplanar spacing of the K saturated specimen. The hydrogen saturated specimen occupies the position that would normally be expected where the soil has previously had a high degree of H saturation. On the other hand, the position of the sodium strongly points to an extremely limited saturation with Na ions. From this discussion, it may appear that these results are of limited value. This is not considered to be the case, since the relative differences in interplanar spacings between the smallest and largest is not great. Moreover, the high degree of swelling and the accompanying large interplanar spacing of this sample, regardless of the amount or type of cation, is a distinct characteristic that is found only in montmorillonite clays (3, 11 and 24).

Other investigators (10) have reported that the character of the innermost ring of montmorillonites is an indication of the nature of the adsorbed ion, that is, a sharp ring denotes that a clay is saturated with only one ion, whereas a broad diffuse ring indicates saturation with a mixture of ions. The variations in the character of the inner ring as found in this study, were inconclusive, unless it can be said that the specimens were primarily saturated with hydrogen ion with a limited amount of the basic ions. This conclusion is partially substantiated by the findings of certain previous investigators (10, 11, 13, 21, 22 and 24).

DISCUSSION OF STANDARD X-RAY DIFFRACTION PATTERNS

The standard diffraction patterns produced in this investigation as shown in APPENDIX B are sufficiently varied among the principal clay mineral families to suggest easy identification of an unknown clay mineral by comparison with the aforementioned standard diffraction patterns. In

view of the overlap of interplanar spacings in the oven dried state, it seems necessary to prepare specimens of the unknown in both an oven dried and hydrated form. In addition, to aiding identification, this procedure would permit an evaluation of the swelling characteristics of the unknown clay sample.

It is not considered that the data obtained for the homo-ionic saturated Illite and Montmorillonite, (Bentonite) specimens is sufficiently conclusive to permit positive identification of the type of ionic saturation; however, it is questioned whether the possibility of finding a one hundred percent homo-ionic saturated clay in nature is sufficient to justify such a comparison. Further, such a comparison for clays saturated with different ions whose valence and dehydrated and hydrated radii are similar, such as Mg^{+4} and Ca^{+1} might prove misleading.

The Hanawalt method (10 and 15) of identification of clay minerals by comparison of interplanar spacings and intensities with those given on the limited number of available ASTM Index cards, was used for all samples investigated except Illite for which no cards are available. Inasmuch as the cards did not give any indication of the moisture content, ion content or origin of the clay mineral, such comparison was necessarily difficult. Based on the assumption that the cards were prepared for oven dried samples, comparisons were made with oven dried diffraction patterns obtained from this investigation. An illustration of this method with the comparisons made in this study is given in APPENDIX C. It might be stated that Schieltz (10) reports that comparisons within $\pm$ 0.05 A should be considered as being satisfactory. Schieltz further reports that intensities of lines are effected to a considerable degree by the relative amount of exposure. It will be noted that in the case of Halloysite,

Montmorillonite Gouge Clay and Montmorillonite Bentonite, the comparisons are only approximate. This is probably due to unavailability of index cards for specific samples used in this work or sufficient cards to obtain an adequate cross-section of the many variations found in each mineral.

EVALUATION OF THE TECHNIQUE EMPLOYED BY DEARTH AND WILLIAMS

In general, the technique used by Dearth and Williams appeared to be satisfactory. A brief discussion of the principal changes and/or suggested improvements employed in this investigation is as follows:

(1) CENTRIFUGING

The centrifuge was found to be an invaluable aid in materially reducing the time required to prepare sample specimens. This improvement eliminated any need for filtering. In addition to the time consideration, centrifuging removed the problem of losing fines thru their being retained on the filter paper.

(2) LOSS OF MOISTURE IN HYDRATED SAMPLES

The procedure of storing plastic tubes containing the hydrated specimen in test tubes filled with distilled water reduced the time consumption in specimen preparation and preserved the samples in a hydrated state for an indefinite period. This technique permitted greater flexibility in X-raying the specimens.

(3) PREPARATION OF PLASTIC TUBES

It is believed that slightly larger tubes, 0.025 inches, gives equally accurate and better definition in the diffraction patterns. These larger tubes also have the advantage of being more rugged and easy to handle.

(4) SUBSTITUTION OF COLLODION FOR DUCO CEMENT IN PREPARATION OF THE EXTRUDED SAMPLES

This consideration is somewhat minor, but the fact that collodion is more fluid and sets up more rapidly makes it easier to handle and justifies its use.

IDENTIFICATION OF CERTAIN UNKNOWN CLAY MINERALS:

An analysis of the diffraction patterns of four unknown samples, specimens of which were prepared in the oven dried and hydrated "as received" states with a discussion concerning their identity is presented as follows:

(a) Corning Hill Area, Intersection New York State Thruway and U. S. Route 9W (82 foot depth)

State	Maximum Interplanar Spacing
Oven Dried	4.01 A
Hydrated	4.24 A

(b) Corning Hill Area, Intersection New York State Thruway and U. S. Route 9W (152 foot depth)

State	Maximum Interplanar Spacing
Oven Dried	4.38 A
Hydrated	4.51 A

(c) Oil Mill Hill (Refractory Clay Bleau Brickyard) Troy, New York (15 foot depth)

State	Maximum Interplanar Spacing
Oven Dried	4.41 A
Hydrated	4.56 A

(d) New R.P.I. Dormitory Area, Burdette Avenue, Troy, New York (15 foot depth)

State	Maximum Interplanar Spacing
Oven Dried	4.39 A
Hydrated	4.43 A

It will be observed that none of the unknown clay samples indicate a large interplanar spacing suggesting the absence of an inner ring. The presence or absence of this inner ring was considered so significant, and will be brought out later, that every means possible was used to confirm its presence. Slow runs on the densitometer, a device for determining the density of the lines, indicated that none of the four samples had a trace of an inner ring. Further, that the swelling characteristics of these clays as they exist in nature is minimum. This study indicated that the interplanar spacings of the four unknown samples lie in a very limited range. Consequently, they will be treated as a group for identification purposes. A comparison of the diffraction patterns with the standard patterns prepared in this investigation immediately suggests the presence of Illite, which has a predominance of ions possessing low swelling characteristics such as calcium. This initial clue is further borne out by the rather grainy pattern obtained from the four samples, which is in agreement with the results of previous investigators. It may be stated that this grainy appearance of the diffraction pattern was not found in any mineral other than Illite which was studied during this investigation. The lack of an inner ring, which is normally obtained from relatively pure Illite samples, indicates the presence of other types of clay minerals, which are either masking or materially effecting the patterns obtained. The small amount of swelling and small interplanar spacing leads to the conclusion that the Illite must be mixed with considerable quantities of Kaolinite which in itself has no swelling characteristics. This is further substantiated by the fact that previous investigators (21) have found that even small quantities of Montmorillonite, due to the small size particles and loose bond between crystals, causes noticeable swelling effects in the clay mineral when these are present.

This conclusion appears to be reasonable inasmuch as the four samples were all obtained within an area of eight miles coupled with the fact that the clay minerals underlying the entire Hudson Valley were formed from marine deposits.

This discussion underlines statements made by many previous workers in X-ray diffraction (2, 10, 17 and 20), that the X-ray diffraction method is not in itself a solution to all soil studies or, for that matter, for identification alone. Its use is considerably enhanced if used in conjunction with other methods, such as spectrographic, microscopic, differential thermal analysis and chemical procedures. This is especially true for investigations of certain types of complex minerals or mixtures. Previous investigators have often found it necessary to purify complex samples prior to using X-ray diffraction methods. It has been found that optical data from microscopic measurements can materially reduce the time and labor by aiding in the selection of the standard pattern to be used in comparison. Nature, in forming crystals, often indiscriminately utilized any available atoms or ions which are reasonably similar in size so long as the structure is kept in equilibrium. Thus, we have crystals with numerous substitutions, which are referred to as "half-breed" depending on the mechanism by which the structure maintains neutrality and perpetuates itself. As a result of such partial substitutions, the refractive indices must be expressed as ranges rather than in terms of definite values. This variation in chemical composition with resulting changes in lattice dimensions causes differences in line intensities, shifting of lines, appearance or disappearance of lines and other changes in X-ray diffraction patterns. Thus, the establishment of a standard set of patterns from certain naturally occuring and commonly found clay minerals serves only to provide a starting point in any identification work.

In the preceeding section, a brief discussion was given concerning efforts to identify sample sediments obtained from various oil bearing sediments underlying the U. S. Naval Shipyard, California. Study of these sediments indicated a predominance of Quartz, Mica and other unweathered primary particles in the fine sand and silt range of particle sizes. For all practical purposes, there is evidently complete absence of active material in the form of secondary mineral (clay) particles.

It has been adequately demonstrated that sand and silt possess little surface activity, and therefore, contribute little to many of the physical characteristics of soils (11). This small surface activity may be attributed not only to a relatively low specific surface when compared with clay particles, but also to the chemical and mineralogical nature of these coarser separates. It is concluded, therefore, that the sample sediments are primarily quartz or other unweathered primary minerals, and that there would not be exhibited any marked physical or chemical activity due to their presence.

From the foregoing, it appears that the introduction of either raw, or chemically treated sea water into these sediments would not result in appreciable swelling or reduction in permeability. It appears, therefore, that there will be little or no effect upon the permeability of these sediments under a program of water repressuring which has been proposed as a remedial measure in connection with the land subsidence in this area.

APPENDIX A

Tabulation of Interplanar Spacings

Bedford, Indiana - Halloysite (H-12)

Type of Homo-Ion	Specimen State	Ring Number 1	2	3	4	5	6	7	8	9	10	11	12	13	14
As Received	Oven Dry	7.30	4.88	4.55	3.63	2.57	2.34	2.23	2.03	1.81	1.67	1.49	1.29	1.23	
	Hydrated	7.30	4.34	3.55	2.52	2.26	1.93	1.62	1.45	1.26	1.21				
Hydrogen	Oven Dry	7.29	4.73	4.34	3.54	2.51	2.26	2.19	1.97	1.76	1.63	1.46	1.26	1.19	
	Hydrated	7.29	4.51	3.64	2.59	2.34	1.63	1.49	1.29	1.24					
Sodium	Oven Dry	7.48	4.48	3.68	2.60	2.38	2.28	2.06	1.83	1.69	1.50	1.29	1.25		
	Hydrated	7.48	4.38	3.62	2.55	2.35	1.67	1.48	1.27	1.23					
Potassium	Oven Dry	7.30	4.74	4.38	3.59	2.55	2.32	2.24	2.01	1.79	1.65	1.47	1.37	1.28	1.22
	Hydrated	7.52	4.89	4.53	3.67	2.64	2.38	1.68	1.50	1.30	1.24				
Calcium	Oven Dry	7.12	4.68	4.29	3.53	2.51	2.25	2.15	1.96	1.76	1.63	1.45	1.26	1.20	
	Hydrated	7.30	4.51	3.62	2.68	2.38	2.03	1.69	1.51						

Macon, Georgia - Kaolinite (H-4)

Type of Homo-Ion	Specimen State	Ring Number 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
As Received	Oven Dried	7.20	4.32	3.57	2.78	2.55	2.32	2.21	1.99	1.94	1.87	1.83	1.78	1.66	1.62	1.58	1.31
	Hydrated	6.9	4.23	3.50	2.48	2.27	1.94	1.68	1.51	1.45	1.21						
Hydrogen	Oven Dried	7.38	4.41	3.64	2.56	2.34	2.01	1.96	1.91	1.84	1.80	1.68	1.63	1.59	1.55	1.50	1.27
	Hydrated	7.20	4.45	3.66	3.17	2.58	2.40	2.03	1.67	1.56	1.51						
Sodium	Oven Dried	7.88	6.98	4.34	3.56	2.52	2.32	1.97	1.87	1.82	1.77	1.65	1.61	1.55	1.54	1.48	1.45
	Hydrated	7.59	6.62	4.35	3.73	3.49	2.58	2.35	2.14	1.67	1.51	1.29	1.24	1.19			
Potassium	Oven Dried	7.21	4.27	3.62	3.27	2.55	2.02	1.68	1.50	1.37	1.23						
	Hydrated	7.19	4.35	3.84	3.50	2.78	2.50	2.31	2.24	1.96	1.76	1.65	1.48	1.29	1.27	1.23	
Calcium	Oven Dried	7.28	4.47	3.63	3.11	2.84	2.58	2.37	2.02	1.68	1.56	1.52	1.32	1.30	1.25	1.20	
	Hydrated	7.24	4.34	3.62	2.41	2.34	2.01	1.67	1.50	1.34	1.24						

Morris , Illinois - Illite (H-36)

Type of Homo-Ion	Specimen State	Ring Number 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
As Received	Oven Dried	9.06	4.79	4.41	3.31	2.56	2.42	2.27	2.13	1.97	1.80	1.62	1.53	1.49	1.40	1.36
	Hydrated	10.85	5.72	3.48	2.84	2.22	1.78									
Hydrogen	Oven Dried	8.51	4.21	3.57	3.21	2.49	2.34	2.21	2.04	1.92	1.75	1.59	1.49	1.46	1.33	1.26
	Hydrated	9.76	4.46	3.35	2.56	2.39	2.24	2.13	1.96	1.80						
Sodium	Oven Dried	10.48	5.14	4.54	3.45	2.70	2.51	2.31	2.20	2.05	1.87	1.72	1.58	1.55	1.42	1.32
	Hydrated	10.83	4.96	4.32	3.27	2.51	2.38	2.21	2.07	1.93	1.80	1.62	1.50	1.47	1.34	1.27
Potassium	Oven Dried	9.04	4.66	4.40	3.83	3.45	2.52	2.51	2.20	2.09	1.87	1.70	1.58	1.55	1.41	
	Hydrated	9.74	4.38	3.32	2.56	2.40	2.22	2.11	1.95	1.55	1.53	1.49	1.37	1.28		
Calcium	Oven Dried		4.13	4.02	3.22	2.49	2.36	2.20	2.07	1.92	1.85	1.77	1.60	1.48	1.46	1.34
	Hydrated		4.51	3.56	2.61	2.48	2.28	2.16	2.02	1.88	1.85	1.66	1.5[illegible]	1.52	1.40	1.31

Pioche, Nevada - Montmorillonite Gouge Clay (H-32)

Type of Homo-Ion	Specimen State	Ring Number 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
As Received	Oven Dried	14.31	4.41	3.51	3.24	3.00	2.81	2.52	2.26	2.08	1.91	1.87	1.63	1.58	1.55	1.52	1.47
	Hydrated	18.51	4.33	2.47	1.67	1.46											
Hydrogen	Oven Dried	15.15	6.61	4.83	4.33	3.39	2.88	2.44	2.15	1.85	1.62	1.55	1.50	1.45	1.28	1.24	
	Hydrated	18.11	4.49	2.98	2.47												
Sodium	Oven Dried	15.78	4.41	3.63	3.23	2.75	2.50	2.15	1.89	1.[illegible]	1.52	1.49	[illegible]	1.24			
	Hydrated	17.1	4.48	3.52	2.58	1.71	1.51	1.29	1.22								
Potassium	Oven Dried	13.31	4.41	3.45	2.24	2.56	2.44	2.17	1.97	1.67	1.52	1.47	1.29	1.24			
	Hydrated	16.78	4.48	3.53	3.27	2.64	2.48	2.11	1.66								
Calcium	Oven Dried	16.32	4.23	3.40	2.83	2.48	1.62	1.50	1.45	1.26	1.21						
	Hydrated	16.35	4.27	3.38	3.01	2.48	1.83	1.62									

Otay, California - Montmorillonite Bentonite (H-24)

Type of Homo-Ion	Specimen State	Ring Number 1	2	3	4	5	6	7	8	9	10	11	12
As Received	Oven Dried	16.78	4.79	4.19		2.55	2.24	1.69	1.50	1.29	1.25		
	Hydrated	19.10	4.48	3.27	2.56	2.02	1.65	1.48					
Hydrogen	Oven Dried	15.70	4.95	4.70	3.59	2.91	2.62	2.29	2.05	1.75	1.55	1.32	1.27
	Hydrated	18.51	4.61	3.25	2.62	1.73	1.50	1.32					
Sodium	Oven Dried	13.32	5.01	4.69	3.60	2.92	2.66	2.31	2.03	1.75	1.54	1.32	1.28
	Hydrated	15.50	4.51	3.16	2.55	1.71	1.50						
Potassium	Oven Dried	13.71	12.12	4.89	4.52	3.45	2.61	2.28	1.70	1.51	1.30		
	Hydrated	20.98	10.05	4.49	3.14	2.56	1.67	1.48	1.32	1.27			
Calcium	Oven Dried	11.52	4.61	3.57	2.86	2.62	2.27	2.04	1.70	1.53	1.31	1.27	
	Hydrated	17.75	4.27	3.90	3.05	2.44	1.44	1.25	1.20				

Corning Hill Area, Intersection - New York State Thruway and U. S. Route 9W (82' depth)

Type of Homo-Ion	Specimen State	Ring Number 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
As Received	Oven Dried	4.01	3.19	3.04	2.90	2.76	2.49	2.32	2.20	2.03	1.90	1.75	1.58	1.49	1.46	1.33
	Hydrated	4.24	3.29	2.89	2.54	2.37	1.77	1.65	1.35	1.26						

Corning Hill Area, Intersection - New York State Thruway and U. S. Route 9W (152' depth)

Type of Homo-Ion	Specimen State	Ring Number 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
As Received	Oven Dried	4.38	3.83	3.42	2.62	2.51	2.31	2.19	2.04	1.88	1.69	1.55	1.53	1.40	1.32	1.27
	Hydrated	4.51	3.32	3.13	2.61	2.50	2.29	2.16	1.97	1.81						

Oil Mill Hill (Refractory Clay, Bleau Brickyard) Troy, N. Y. (15' depth)

Type of Homo-Ion	Specimen State	Ring Number 1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Oven Dried	4.41	4.21	3.70	3.31	3.19	2.98	2.85	2.56	2.42	2.25	2.11	1.97	1.88	1.37
As Received	Hydrated	4.56	3.18	2.86	2.77	2.45	2.28	2.17	2.02	1.86	1.73	1.62	1.58	1.48	1.24

R.P.I. Dormitory Area (Burdette Avenue) Troy, N. Y. (15' depth)

Type of Homo-Ion	Specimen State	Ring Number 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
	Oven Dried	4.39	3.38	3.24	3.09	2.89	2.66	2.56	2.54	2.33	2.17	2.03	1.90	1.86	1.70	1.57
As Received	Hydrated	4.43	3.91	2.98	2.82	2.66	2.50	2.18	2.07	1.98	1.87					

APPENDIX B

Diffraction Patterns

Halloysite - As Received - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.595	1	7.30
2	.905	10	4.88
3	.995	2	4.55
4	1.22	3	3.63
5	1.73	5	2.57
6	1.905	6	2.34
7	2.02	11	2.23
8	2.205	12	2.03
9	2.50	13	1.81
10	2.73	7	1.67
11	3.11	4	1.49
12	3.655	8	1.29
13	3.84	9	1.23

Halloysite - As Received - Hydrated

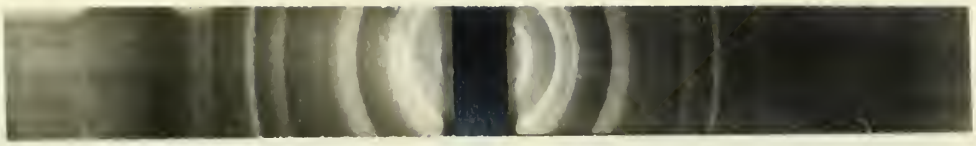
Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.60	2	7.30
2	1.02	1	4.34
3	1.25	4	3.55
4	1.77	5	2.52
5	1.975	6	2.26
6	2.325	10	1.93
7	2.81	7	1.62
8	3.185	3	1.45
9	3.74	8	1.26
10	3.935	9	1.21

Halloysite - H Saturated - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.61	1	7.29
2	.935	12	4.73
3	1.02	2	4.34
4	1.245	3	3.54
5	1.775	5	2.51
6	1.97	6	2.26
7	2.05	13	2.19
8	2.275	10	1.97
9	2.545	11	1.76
10	2.79	7	1.63
11	3.17	4	1.46
12	3.73	8	1.26
13	3.975	9	1.19

Halloysite - H Saturated - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.61	2	7.29
2	.98	1	4.51
3	1.21	4	3.64
4	1.72	5	2.59
5	1.905	6	2.34
6	2.695	7	1.68
7	3.095	3	1.49
8	3.655	8	1.29
9	3.815	9	1.24



Halloysite - Na Saturated - Oven Dry

Ring. No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.59	1	7.48
2	.99	2	4.48
3	1.195	3	3.68
4	1.715	5	2.60
5	1.875	6	2.38
6	1.955	10	2.28
7	2.175	11	2.06
8	2.46	12	1.83
9	2.69	7	1.69
10	3.07	4	1.50
11	3.62	8	1.29
12	3.78	9	1.25

Halloysite - Na Saturated - Hydrated

Ring. No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.59	2	7.48
2	1.01	1	4.38
3	1.22	3	3.62
4	1.745	6	2.55
5	1.895	5	2.35
6	2.73	7	1.67
7	3.13	4	1.48
8	3.72	8	1.27
9	3.86	9	1.23

Halloysite - K Saturated - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.60	1	7.30
2	.93	13	4.74
3	1.01	2	4.38
4	1.23	3	3.59
5	1.745	5	2.55
6	1.925	6	2.32
7	2.02	10	2.24
8	2.245	11	2.01
9	2.525	12	1.79
10	2.76	7	1.65
11	3.145	4	1.47
12	3.41	19	1.37
13	3.69	8	1.28
14	3.885	9	1.22

Halloysite - K Saturated - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.585	2	7.52
2	.90	8	4.89
3	.975	1	4.53
4	1.20	4	3.67
5	1.69	5	2.64
6	1.875	6	2.38
7	2.695	7	1.68
8	3.07	3	1.50
9	3.615	9	1.30
10	3.805	10	1.24

Halloysite - Ca Saturated - Oven Dry

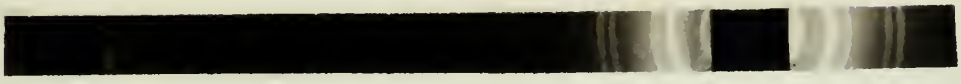
Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.615	1	7.12
2	.95	10	4.68
3	1.03	2	4.29
4	1.25	3	3.53
5	1.780	6	2.51
6	1.975	5	2.25
7	2.085	11	2.15
8	2.295	12	1.96
9	2.57	13	1.76
10	2.80	7	1.63
11	3.195	4	1.45
12	3.75	8	1.26
13	3.935	9	1.20

Halloysite - Ca Saturated - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.60	3	7.30
2	.98	1	4.51
3	1.215	2	3.62
4	1.655	4	2.68
5	1.87	5	2.38
6	2.21	8	2.03
7	2.69	6	1.69
8	3.05	7	1.51

Kaolinite - As Received - Oven Dried

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.61	2	7.20
2	1.025	1	4.41
3	1.235	3	3.57
4	1.755	4	2.55
5	1.925	5	2.32
6	2.265	8	1.99
7	2.32	9	1.94
8	2.41	10	1.87
9	2.475	11	1.825
10	2.55	12	1.78
11	2.75	7	1.66
12	3.10	6	1.490
13	3.59	13	1.31
14	3.625	14	1.30
15	3.83	15	1.24



Kaolinite - As Received - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.635	1	6.9
2	1.045	2	4.23
3	1.265	3	3.50
4	1.805	4	2.48
5	1.965	5	2.27
6	2.32	8	1.94
7	2.81	7	1.625
8	3.06	9	1.51
9	3.19	6	1.45
10	3.91	10	1.21

Kaolinite - H Saturated - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.605	2	7.38
2	1.0	1	4.41
3	1.22	3	3.64
4	1.745	4	2.56
5	1.905	5	2.34
6	2.245	8	2.01
7	2.295	9	1.96
8	2.36	10	1.91
9	2.45	11	1.84
10	2.515	12	1.80
11	2.72	7	1.68
12	3.08	6	1.50
13	3.555	15	1.32
14	3.71	13	1.27
15	3.80	14	1.245

Kaolinite - H Saturated - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.61	2	7.2
2	.995	1	4.45
3	1.205	3	3.66
4	1.39	10	3.17
5	1.725	4	2.58
6	1.865	5	2.40
7	2.21	8	2.03
8	2.72	6	1.67
9	2.94	9	1.56
10	3.06	7	1.51

Kaolinite - Na Saturated - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.559	4	7.88
2	.63	3	6.98
3	1.02	2	4.34
4	1.24	1	3.56
5	1.77	6	2.52
6	1.925	5	2.32
7	2.28	11	1.97
8	2.755	7	1.65
9	2.835	9	1.61
10	2.005	10	1.54
11	3.115	8	1.48
12	3.52	15	1.33
13	3.62	14	1.30
14	3.68	13	1.28
15	3.835	12	1.23

Kaolinite - Na Saturated - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.58	3	7.59
2	.66	2	6.62
3	1.015	1	4.35
4	1.18	11	3.73
5	1.265	10	3.49
6	1.73	4	2.58
7	1.895	5	2.35
8	2.210	8	2.14
9	2.73	7	1.67
10	3.07	6	1.51
11	3.65	9	1.29
12	3.81	12	1.24
13	3.97	13	1.79

Kaolinite - K Saturated - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.62	2	7.21
2	1.035	1	4.27
3	1.215	3	3.62
4	1.35	4	3.27
5	1.75	5	2.55
6	1.90	6	2.35
7	2.23	9	2.02
8	2.71	7	1.68
9	3.08	8	1.50
10	3.40	10	1.37
11	3.83	11	1.23

Kaolinite - K Saturated - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.61	1	7.19
2	1.015	2	4.35
3	1.145	15	3.84
4	1.24	3	3.56
5	1.60	14	2.78
6	1.78	4	2.50
7	1.935	5	2.31
8	2.005	13	2.24
9	2.29	8	1.96
10	2.57	12	1.76
11	2.76	6	1.65
12	3.12	7	1.48
13	3.63	11	1.29
14	3.70	10	1.27
15	3.845	9	1.23

Kaolinite - Ca Saturated - Oven Dry

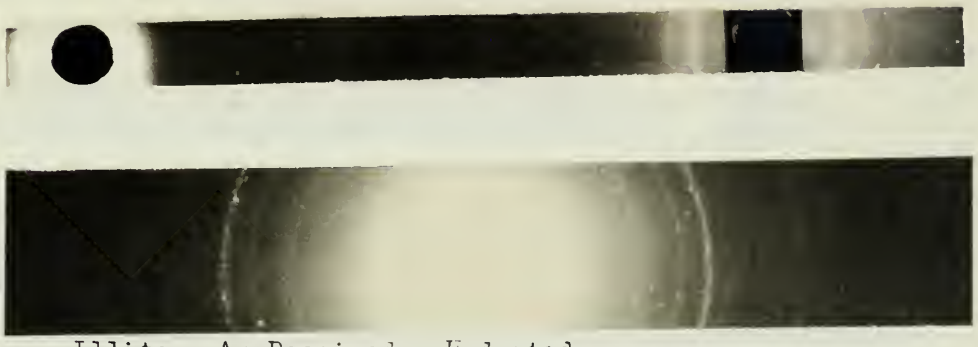
Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.605	3	7.28
2	.99	1	4.47
3	1.215	2	3.63
4	1.42	14	3.11
5	1.56	15	2.84
6	1.73	4	2.58
7	1.885	5	2.37
8	2.225	8	2.02
9	2.70	7	1.68
10	2.93	12	1.56
11	3.04	6	1.52
12	3.53	11	1.32
13	3.605	9	1.30
14	3.765	10	1.25
15	3.945	13	1.20

Kaolinite - Ca Saturated - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.615	2	7.24
2	1.02	1	4.34
3	1.22	3	3.62
4	1.86	4	2.41
5	1.91	5	2.34
6	2.24	8	2.01
7	2.71	6	1.67
8	3.08	7	1.50
9	3.50	10	1.34
10	3.80	9	1.24

Illite - As Received - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.49	3	9.06
2	.925		4.79
3	1.00	2	4.41
4	1.335	1	3.31
5	1.74	4	2.56
6	1.85	8	2.42
7	1.96		2.27
8	2.12		2.13
9	2.29	10	1.97
10	2.51	9	1.80
11	2.81	6	1.62
12	3.015	7	1.53
13	3.09		1.49
14	3.325		1.40
15	3.42	5	1.36
16	3.655	10	1.29
17	3.795		1.24



Illite - As Received - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.80	3	10.85
2	.965	2	5.72
3	1.27	1	3.48
4	1.56	4	2.84
5	2.00	5	2.22
6	2.53	6	1.78

* Cassette

Illite - H Saturated - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.52	3	8.51
2	1.05	2	4.21
3	1.235		3.57
4	1.375	1	3.21
5	1.795	5	2.49
6	1.905	6	2.34
7	2.04		2.21
8	2.20	9	2.04
9	2.35	8	1.92
10	2.585	7	1.75
11	2.88	12	1.59
12	3.095	11	1.49
13	3.18	10	1.46
14	3.51	4	1.33
15	3.74		1.26
16	3.895		1.22

Illite - H Saturated - Hydrated

	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	.95	3	9.75
	2	.995	2	4.46
	3	1.32	1	3.35
	4	1.74	4	2.56
	5	1.87	6	2.39
	6	2.01	7	2.24
	7	2.12	8	2.13
	8	2.30		1.96
	9	2.51	5	1.80

*Cassette

Illite - Na Saturated - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.42	3	10.48
2	.855		5.14
3	.975	2	4.54
4	1.28	1	3.45
5	1.65	4	2.70
6	1.78		2.51
7	1.93		2.31
8	2.045		2.20
9	2.19	8	2.05
10	2.41	9	1.87
11	2.65	5	1.72
12	2.885		1.58
13	2.98	7	1.55
14	3.285	6	1.42
15	3.535	10	1.32
16	3.685		1.28
17	3.76		1.26
18	3.870		1.22
19	3.94		1.21

Illite - Na Saturated - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.85	5	10.83
2	.89	4	4.96
3	1.025	1	4.32
4	1.35	2	3.27
5	1.785	3	2.51
6	1.88	9	2.38
7	2.04		2.21
8	2.16		2.07
9	2.33	10	1.93
10	2.52		1.80
11	2.82		1.62
12	3.08		1.50
13	3.15	6	1.47
14	3.49	7	1.34
15	3.71	8	1.27

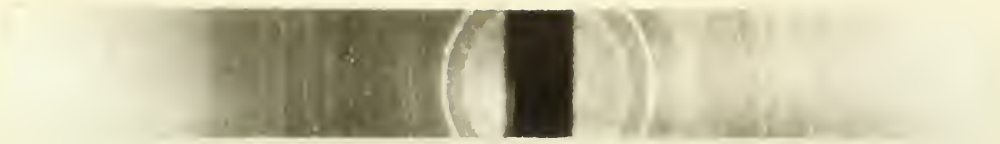
Illite - K Saturated - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.49	4	9.04
2	.95	3	4.66
3	1.005	2	4.40
4	1.15		3.83
5	1.28	1	3.45
6	1.77	5	2.52
7	1.775	6	2.51
8	2.04		2.20
9	2.14	10	2.09
10	2.415	7	1.87
11	2.68	11	1.70
12	2.895		1.58
13	2.975	8	1.55
14	3.29	9	1.41

Illite - K Saturated - Hydrated

*	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	.95	2	9.74
	2	1.01	3	4.38
	3	1.33	1	3.32
	4	1.745	4	2.56
	5	1.86	7	2.40
	6	2.00	8	2.22
	7	2.125	9	2.11
	8	2.31	10	1.95
	9	2.965	11	1.55
	10	3.02	12	1.53
	11	3.10	5	1.49
	12	3.42	6	1.37
	13	3.69	13	1.28

* Cassette



Illite - Ca Saturated - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	---	---	---
2	1.07	3	4.13
3	1.095	2	4.02
4	1.37	1	3.22
5	1.795	4	2.49
6	1.895	5	2.36
7	2.045		2.20
8	2.17		2.07
9	2.355		1.92
10	2.45		1.85
11	2.565	10	1.77
12	2.85	6	1.60
13	3.085	9	1.49
14	3.17	8	1.46
15	3.48	7	1.34
16	3.735	11	1.26
17	3.885	--	1.22

Illite - Ca Saturated - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	---	--	----
2	.985	2	4.51
3	1.24	1	3.56
4	1.705	3	2.61
5	1.805	4	2.48
6	1.96	5	2.28
7	2.08	6	2.16
8	2.225	7	2.02
9	2.39	8	1.88
10	2.44	9	1.85
11	2.74	10	1.66
12	2.91	11	1.57
13	3.02	12	1.52
14	3.33	13	1.40
15	3.59	14	1.31

Montmorillonite (Gouge Clay)-As Received - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
* 1	.645	1	14.31
2	1.00	2	4.41
3	1.26	4	3.51
4	1.36		3.24
5	1.475	5	3.00
6	1.58		2.81
7	1.77	3	2.52
8	1.97		2.26
9	2.16		2.08
10	2.36		1.91
11	2.415		1.87
12	2.79	8	1.63
13	2.855		1.58
14	2.975	7	1.55
15	3.04	6	1.52
16	3.145	9	1.47
17	3.295		1.41

*

Montmorillonite (Gouge Clay)-As Received - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
* 1	.50	1	18.51
2	1.02	2	4.33
3	1.805	3	2.47
4	2.76	5	1.67
5	3.17	4	1.46

*

*Cassette

Montmorillonite (Gouge Clay) - H Saturated -
Oven Dry

	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	.605	1	15.15
	2	.66	9	6.61
	3	.925		4.83
	4	1.02	2	4.33
	5	1.305	6	3.39
	6	1.535		2.88
	7	1.83	3	2.44
	8	2.09		2.15
	9	2.45	11	1.85
	10	2.81	10	1.62
	11	2.955		1.55
	12	3.085	5	1.50
	13	3.20	4	1.45
	14	3.685	7	1.28
	15	3.825	8	1.24

*

Montmorillonite (Gouge Clay) - H Saturated -
Hydrated

	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	.51	1	18.11
	2	.98	2	4.49
	3	1.48	3	2.98
	4	1.805	4	2.47

*

* Cassette

Montmorillonite (Gouge Clay) - Na Saturated - Oven Dry

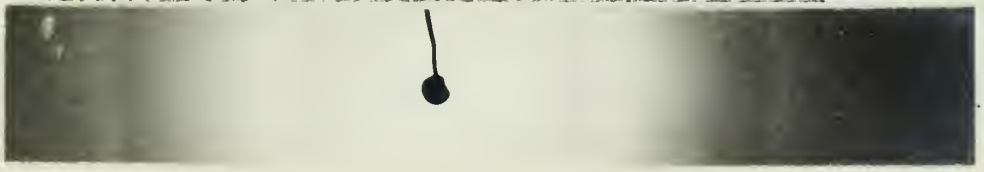
Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.585	1	15.78
2	1.00	2	4.41
3	1.215		3.63
4	1.365		3.23
5	1.615		2.75
6	1.79	3	2.50
7	2.085		2.15
8	2.385		1.89
9	2.72	6	1.67
10	3.04		1.52
11	3.11	4	1.49
12	3.67	5	1.28
13	3.83	7	1.24

*

Montmorillonite (Gouge Clay) - Na Saturated - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.54	1	17.1
2	.99	2	4.48
3	1.255		3.52
4	1.725	3	2.58
5	2.67	4	1.71
6	3.05	5	1.51
7	3.64		1.29
8	3.87		1.22

*



* Cassette

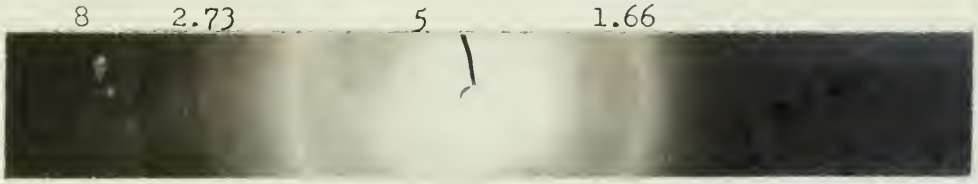
Montmorillonite (Gouge Clay) - K Saturated -
Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
* 1	.695	1	13.31
2	1.00	2	4.41
3	1.28		3.45
4	1.36		3.24
5	1.735	3	2.56
6	1.83		2.44
7	2.07		2.17
8	2.28	5	1.97
9	2.72	7	1.67
10	3.03	4	1.52
11	3.15	6	1.47
12	3.65		1.29
13	3.81		1.24

*

Montmorillonite (Gouge Clay) - K Saturated)
Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
* 1	.515	1	16.78
2	.99	2	4.48
3	1.25	3	3.53
4	1.35	4	3.27
5	1.685		2.64
6	1.80		2.48
7	2.13		2.11
8	2.73	5	1.66



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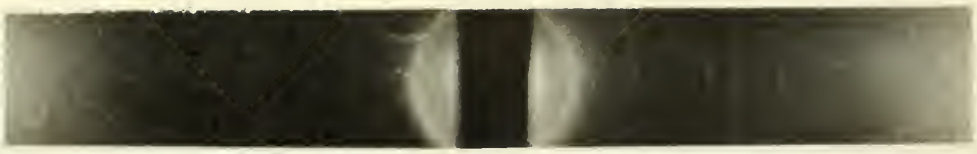
* Cassette



Montmorillonite (Gouge Clay) - Ca Saturated - Oven Dry

	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	.57	1	16.32
	2	1.045	2	4.23
	3	1.30	6	3.40
	4	1.51	7	2.83
	5	1.80	3	2.48
	6	2.81		1.62
	7	3.07	5	1.50
	8	3.185	4	1.45
	9	3.755		1.26
	10	3.915		1.21

*

Montmorillonite (Gouge Clay) - Ca Saturated - Hydrated

	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	.565	1	16.35
	2	1.0335	2	4.27
	3	1.31	3	3.38
	4	1.47	4	3.01
	5	1.805	5	2.48
	6	2.47	6	1.83
	7	2.82	7	1.62

*

* Cassette

Montmorillonite (Bentonite) - As Received - Oven Dry

	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	.55	1	16.78
	2	.92	7	4.79
	3	.985	2	4.19
	4			
	5			
	6	1.745	4	2.55
	7	1.99	8	2.24
	8	2.70		1.69
	9	3.07	3	1.50
	10	3.63	5	1.29
	11	3.785	6	1.25

*

Montmorillonite (Bentonite) - As Received - Hydrated

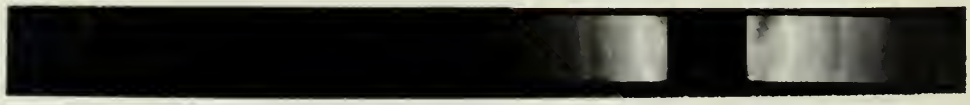
	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	.485	1	19.10
	2	.99	2	4.48
	3	1.35	3	3.27
	4	1.745	4	2.56
	5	2.22	5	2.02
	6	2.77	6	1.65
	7	3.12	7	1.48

*

* Cassette

Montmorillonite (Bentonite) - H Saturated - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
* 1	.59		15.70
2	.89		4.95
3	.945	1	4.70
4	1.23	7	3.59
5	1.525	8	2.91
6	1.69	2	2.62
7	1.945		2.29
8	2.195		2.05
9	2.60	5	1.75
10	2.98	3	1.55
11	3.55	4	1.32
12	3.71	6	1.27



Montmorillonite (Bentonite) - H Saturated - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
* 1	.50	1	18.51
2	.96	2	4.61
3	1.36	5	3.25
4	1.70	3	2.62
5	2.615	6	1.73
6	2.98	4	1.50
7	3.54	7	1.32

* Cassette

Montmorillonite (Bentonite) Na Saturated -
Oven Dry

	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	.695	1	13.32
	2	.88	11	5.01
	3	.945	2	4.69
	4	1.225	9	3.60
	5	1.515	8	2.92
	6	1.67	3	2.66
	7	1.93	10	2.31
	8	2.21	12	2.03
	9	2.595	5	1.75
	10	2.985	4	1.54
	11	3.54	6	1.32
	12	3.695	7	1.28

*

Montmorillonite (Bentonite) - Na Saturated
Hydrated

	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	.595	1	15.50
	2	.985	2	4.51
	3	1.40	6	3.16
	4	1.75	4	2.55
	5	2.66	5	1.11
	6	3.07	3	1.50

*

* Cassette

Montmorillonite (Bentonite) - K Saturated -
Oven Dry

	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	.675	1	13.71
	2	.36		12.12
	3	.90		11.89
	4	.98	2	4.52
	5	1.28		3.45
	6	1.71	3	2.61
	7	1.96		2.28
	8	2.685	5	1.70
	9	3.05	4	1.51
	10	3.62	6	1.30

*

Montmorillonite (Bentonite) K Saturated -
Hydrated

	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	.42	1	20.98
	2	.99	2	4.49
	3	1.405	5	3.14
	4	1.74	3	2.56
	5	2.72	6	1.67
	6	3.11	4	1.49
	7	3.56	7	1.32
	8	3.72	8	1.27

*

* Cassette

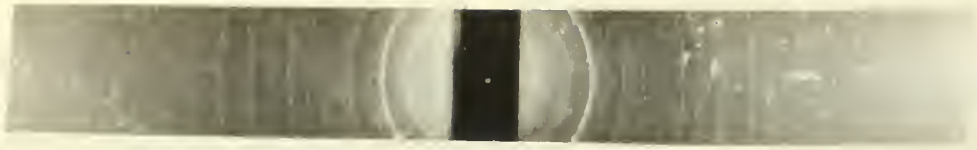
Montmorillonite (Bentonite) Ca Saturated - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.38	1	11.52
2	.96	2	4.61
3	1.235	8	3.57
4	1.55		2.86
5	1.70	3	2.62
6	1.96		2.27
7	2.20		2.04
8	2.665	5	1.70
9	3.01	4	1.53
10	3.57	6	1.31
11	3.73	7	1.27

Montmorillonite (Bentonite) Ca Saturated - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
* 1	.52	1	17.75
2	1.035	2	4.27
3	1.13		3.90
4	1.45	5	3.05
5	1.825	3	2.44
6	3.22	4	1.44
7	3.79		1.25
8	3.97		1.20

* Cassette



Corning Hill Area Intersection, New York Thruway and U. S. Route 9W, Albany County, N. Y. (82' depth)
As Received - Oven Dry

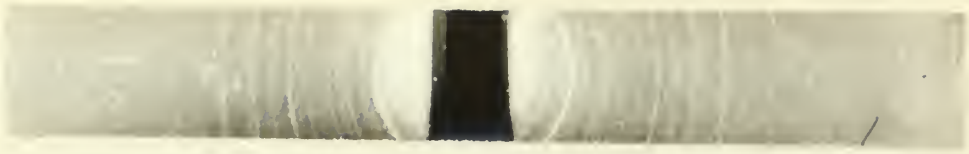
Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	1.10		4.01
2	1.385	1	3.19
3	1.45		3.04
4	1.53		2.90
5	1.61		2.76
6	1.795	5	2.49
7	1.92	8	2.32
8	2.05	7	2.20
9	2.21	6	2.03
10	2.365		1.90
11	2.59	2	1.75
12	2.895		1.58
13	3.10	4	1.49
14	3.175		1.46
15	3.515	3	1.33

*

Corning Hill Area Intersection, New York Thruway and U. S. Route 9W, Albany County, N. Y. (82' depth)
As Received - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	1.04	2	4.24
2	1.345	1	3.29
3	1.535	3	2.89
4	1.76	4	2.54
5	1.885	5	2.37
6	2.56		1.77
7	2.75	8	1.65
8	3.45	7	1.35
9	3.75	6	1.26

* Cassette



Corning Hill Area Intersection, New York Thruway and U. S. Route 9W, Albany County, N. Y. (152' depth)
As Received - Oven Dry

Ring No.	Radius In cm.	Order of Intensity	Interplanar Distance (A)
1	1.01	5	4.38
2	1.15	6	3.83
3	1.29	1	3.42
4	1.685		2.62
5	1.785		2.51
6	1.93		2.31
7	2.05		2.19
8	2.205		2.04
9	2.44	4	1.88
10	2.69		1.69
11	2.955	3	1.55
12	2.995		1.53
13	3.315	2	1.40
14	3.565		1.32
15	3.725		1.27

*

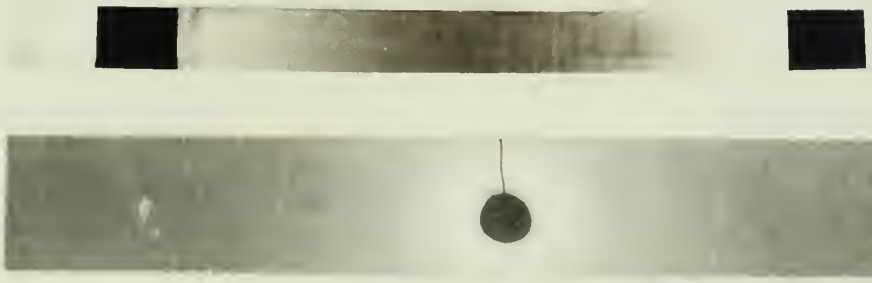
Corning Hill Area Intersection, New York Thruway and U. S. Route 9W, Albany County, N. Y. (152' depth)
As Received - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.98	1	4.51
2	1.32		3.32
3	1.41		3.13
4	1.71	3	2.61
5	1.79	4	2.50
6	1.95		2.29
7	2.08		2.16
8	2.26		1.97
9	2.49	2	1.81

* Cassette

Oil Mill Hill (Refractory Clay, Bleau Brickyard), Troy, N.Y.
(15' depth) As Received--Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	1.00	2	4.41
2	1.05		4.21
3	1.19		3.70
4	1.335	1	3.31
5	1.385	10	3.19
6	1.48	9	2.98
7	1.555		2.85
8	1.74	7	2.56
9	1.85	8	2.42
10	1.975		2.25
11	2.13		2.11
12	2.28		1.97
13	2.40		1.88
14	2.52	4	1.80
15	2.75		1.65
16	3.05	5	1.51
17	3.085	6	1.49
18	3.40	3	1.37



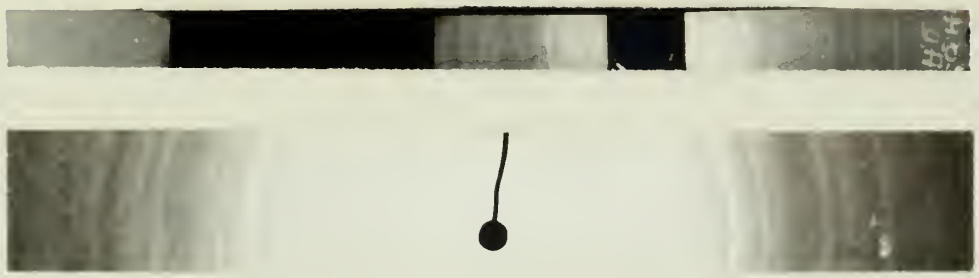
Oil Mill Hill (Refractory Clay, Bleau Brickyard), Troy, N.Y.
(15' depth) As Received - Hydrated

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.97	2	4.56
2	1.39	1	3.18
3	1.55		2.86
4	1.605		2.77
5	1.825	3	2.45
6	1.96	4	2.28
7	2.075	5	2.17
8	2.22	6	2.02
9	2.39	7	1.88
10	2.63		1.73
11	2.83		1.62
12	2.89		1.58
13	2.93		1.5[illegible]
14	3.13		1.4[illegible]
15	3.23		1.[illegible]

* Cassette

New R.P.I. Dormitory Area, Burdette Avenue, Troy, N. Y.
(15' Depth) As Received - Oven Dry

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	1.01	5	4.39
2	1.31	1	3.38
3	1.36		3.24
4	1.43		3.09
5	1.53		2.89
6	1.675	10	2.66
7	1.76	9	2.54
8	1.915	8	2.33
9	2.07	7	2.17
10	2.205	6	2.03
11	2.37		1.90
12	2.43	4	1.86
13	2.675		1.70
14	2.91	3	1.57
15	3.30	2	1.41



New R.P.I. Dormitory Area, Burdette Avenue, Troy, N. Y.
(15' Depth) As Received - Hydrated

	Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
*	1	2.10	5	4.43
*	2	2.375	2	3.91
*	3	3.125	1	2.98
*	4	3.30	4	2.82
*	5	3.50	3	2.66
*	6	3.74		2.50
*	7	4.325		2.18
*	8	4.59		2.07
*	9	4.78		1.98
*	10	5.11		1.87

* Cassette

APPENDIX C

Comparisons of Standard X-ray Diffraction Patterns with ASTM Index Cards

Bedford, Indiana Halloysite (H-12) Diffraction Pattern

Ring No.	Radius in cm.	Order of Intensity	Interplanar Distance (A)
1	.595	1	7.30
2	.905	10	4.88
3	.995	2	4.55
4	1.22	3	3.63
5	1.73	5	2.57
6	1.905	6	2.34
7	2.02	11	2.23
8	2.205	12	2.03
9	2.50	13	1.81
10	2.73	7	1.67
11	3.11	4	1.49
12	3.655	8	1.29
13	3.84	9	1.23

ASTM Card for Halloysite (API-6)

d	4.44	7.21	3.59	7.21
I/I_1	100	60	50	60

$Al_2Si_2O_5(OH_4)$

Halloysite

Rad: $C_uK\alpha$

Filter: Nickel

d in A° $\lambda = 1.539$	I/I_1	d in A°	I/I_1
7.21	60		
4.44	100		
3.59	50		
2.50	25		
2.50	25		
2.33	12		
2.24	12		
1.49	40		
1.24	6		

Poor Patterns with unsatisfactory lines & bands

Macon, Georgia - Kaolinite (H-4) - Diffraction Pattern

Ring No.	Radius in cm.	Order of Intensity	Interplanar Spacing (A)
1	.61	2	7.20
2	1.025	1	4.41
3	1.235	3	3.57
4	1.755	4	2.55
5	1.925	5	2.32
6	2.265	8	1.99
7	2.32	9	1.94
8	2.41	10	1.87
9	2.475	11	1.825
10	2.55	12	1.78
11	2.75	7	1.66
12	3.10	6	1.49
13	3.59	13	1.31
14	3.625	14	1.30
15	3.83	15	1.24

ASTM Index Card for Kaolinite

d	3.59	7.2	4.45
I/I_1	1.0	0.80	0.80
I	12.5	10	10

$Al_2Si_2O_0(OH)_4$

Kaolinite

Z

Ao bo Co

A C

D

n w c

d in A° λ=.708	I/I_1	d in A° λ= .708	I/I_1
7.20	0.80	1.80	0.80
4.45	0.80	1.67	0.40
4.30	0.64	1.54	0.16
4.20	0.48	1.49	0.56
4.04	0.32	1.31	0.08
3.59	1.00	1.289	0.16
2.56	0.48	1.24	0.16
2.50	0.48		
2.34	0.80		
1.99	0.32		
1.90	0.08		
1.85	0.08		

Pioche Nevada, Montmorillonite (Gouge Clay) H-32

Ring No.	Radius in cm.	Order of Intensity	Interplanar Spacing (A)
1	.645	1	14.31
2	1.00	2	4.41
3	1.26	4	3.51
4	1.36		3.24
5	1.475	5	3.00
6	1.58		2.81
7	1.77	3	2.52
8	1.97		2.26
9	2.16		2.08
10	2.36		1.91
11	2.415		1.87
12	2.79	8	1.63
13	2.855		1.58
14	2.975	7	1.55
15	3.04	6	1.52
16	3.145	9	1.47
17	3.295		1.41

ASTM Index Card for Montmorillonite (API-16)

d	14.82	4.43	1.49	14.82
I/I_1	100	80	80	100

$(Al_{1.51}Fe_{.13}Mg_{.40})(Al_{.07}Si_{3.43})$

$O_{10}(OH_2)$ $(Na_{.02}Ca_{.18})$

Montmorillonite

Rad: $C_uK\alpha$

Filter: Nickel

d in A° $\lambda = 1.539$	I/I_1	d in A°	I/I_1
14.82	100		
5.04	30		
4.43	80		
3.06	30		
2.54	50		
2.23	10		
1.68	30		
1.49	80		
1.29	30		
1.24	20	Diffuse	
1.12	10	Pattern	
1.03	10		
0.97	10		
0.87	10		

Otay, California Montmorillonite Bentonite (H-24)
Diffraction Pattern

Ring No.	Radius in cm.	Order of Intensity	Interplanar Spacing (A)
1	.55	1	16.78
2	.92	7	4.79
3	.985	2	4.19
4			
5			
6	1.745	4	2.55
7	1.99	8	2.24
8	2.70		1.69
9	3.07	3	1.50
10	3.63	4	1.29
11	3.785	5	1.25

ASTM Card for Montmorillonite (API-15)

d	15.26	1.50	5.16	15.26
I/I_1	100	80	50	100

$Al_{1.44}Fe_{.08}Mg_{.53})(Al_{.10}Si_{3.90})O_{10}$

$(OH)_2Na_{.02}Ca_{.18})$

Montmorillonite

Rad: $CuK\alpha$

Filter: Nickel

d in A° $\lambda = 1.539$	I/I_1	d in A°	I/I_1
15.26	100		
5.16	50		
4.50	30		
3.87	10		
3.33	10		
3.07	10		
2.24	10		
1.69	30		
1.50	80		
1.29	30		
1.24	30		
1.12	10		
1.03	10		
0.98	10		
0.87	10		

Diffuse Pattern

APPENDIX D
BIBLIOGRAPHY

1. Soil Science 31 (25-55)

2. Kilcawley, E.J.Prof. "The Clay Minerals" unpublished paper-R.P.I., Troy,N.Y.

3. Dearth,K.H and Williams, R.C. "Investigation of Expansion Characteristics of Clays by X-ray Diffraction" (1951), R.P.I., Troy, N. Y.

4. Davey, W.P. "Chemical Analysis by X-Ray Diffraction Methods" ASTM Symposium on Radiography and X-ray Diffraction (1936) Philadelphia, Pa.

5. Civil Engineering November 1949 "Discussion of Land Subsidence of Terminal Island, California"

6. Forbes, H.P. "American Society of Civil Engineers, Proceedings" November 1949

7. Grant & Gillaly "Discussion of Land Subsidence of Terminal Island, California" - American Society of Civil Engineers Proceedings - March 1948

8. Kilcawley, E.J.Prof. "Clay" unpublished paper - R.P.I., Troy, N.Y.

9. Taylor, A. D. "An Introduction to X-ray Metallography" John Wiley & Sons, N. Y.

10. Schieltz, H. Cyril "X-ray Analysis", Symposium on Subsurface Geological Methods" 2nd Edition, Colorado School of Mines, pp. 211-240

11. Baver, L. D. "Soil Physics" John Wiley & Sons, Inc. N. Y.

12. Hosking, J.S. "The Cation Exchange Capacity of Soils and Soil Colloids - Variation with Hydrogen-Ion Concentration" Journal of the Council for Scientific and Industrial Research. Vol. 21 No. 1 - Feb. 1948

13. Jeffries, C.D. & Jackson, M.L. "Mineralogical Analysis of Soils" Soil Science Vol. 68, No. 1-July 1949

14. Marshall, C.E. & Jeffries, C.D. "Mineralogical Methods in Soil Research - Part I The Correlation of Soil Types on Parent Materials with Supplementary Information on Weathering Processes" Soil Science Society of America - Proceedings 1945, Vol. 10

15. Reference Clay Materials API Research Project 49, Columbia University.

16. Bragg, W. L. "Atomic Structure of Minerals", Cornell University Press, Ithaca, N. Y.

17. Hauser, Ernest A. "Colloidal Phenomena" McGraw-Hill Book Co., Inc. N. Y. (1939)

18. Jenkins, and While "Fundamentals of Physical Optics" First Edition N. Y., McGraw-Hill 1939

19. Kelley, W. P. "Cation Exchange in Soils" American Soil Science Monograph Series No. 109

20. Hellman, M. N. Aldrich, D. C. & Jackson, M.C. "Further notes on X-ray Diffraction Procedure for Positive Differentiation of Montmorillonite and Hydrous Mica" Soil Science Society of America - Proceedings 7 (194-200) (1942)

21. Bradley, W. F. "Diagnostic Criteria for Clay Minerals" American Mineralogist 30(1945) Urbana, Illinois

22. Bradley, W. F. "Molecular Associations Between Montmorillonite, Some Polyfunctional Organic Liquids" Journal of American Chemical Society, Vol. 67 No. 6/45, Urbana, Illinois

23. Barshad, J. "The Effect of the Interlayer Cations on the Expansion of the Mica Type of Crystal Lattice" American Mineralogist, Vol. 35, pp. 225 1950

24. Ross, C. A. and Hendricks, S.B. "Minerals of the Montmorillonite Group" Geological Survey-Professional paper 20513 U. S. Geological Survey, 1945

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